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DEVELOPMENT DOCUMENT FOR EFFLUENT LIMITATIONS GUIDELINES AND NEW SOURCE PERFORMANCE STANDARDS FOR THE SYNTHETIC POLYMER SEGMENT OF THE PLASTICS AND SYNTHETIC MATERIALS MANUFACTURING POINT SOURCE CATEGORY

ENVIRONMENTAL PROTECTION AGENCY

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This document presents the findings of an extensive study of the Synthetic Polymers Segment of the Plastics and Synthetic Materials Manufacturing Point Source Category for the purpose of developing effluent limitations, guidelines, standards of performance for new sources, and pretreatment standards for the industry in compliance with and to implement Sections 301, 304 and 306 of the Federal Water Pollution Control Act Amendments of 1972.

Effluent limitations guidelines contained herein set forth as mandated by the "Act":

(1) The degree of effluent reduction attainable through the application of the "best practicable control technology currently available" which must be achieved by nonnew point sources by no later than July 1, 1977.

(2) The degree of effluent reduction attainable through the application of the "best available technology economically achievable" which must be achieved by nonnew point sources by no later than July 1, 1983.

The standards of performance for new sources contained herein set forth the degree of effluent reduction which is achievable through the application of the "best available demonstrated control technology, process, operating methods, or other alternatives."

This report contains findings, conclusions and recommendations on control and treatment technology relating to chemical wastes from the manufacture of 15 different plastic and synthetic polymers. Supporting data and rationale for development of the effluent limitations, guidelines and standards of performance are contained herein.

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ABSTRACT

This development document presents the findings of an extensive study of the synthetic polymers segment of the plastics and synthetics industry for the purposes of developing effluent limitations guidelines, and standards of performance for the industry to implement Sections 304, 306, and 307 of the Federal Water Pollution Control Act of 1972 (PL 92-500). Guidelines and standards were developed for the following major products:

Ethylene-Vinyl Acetate Copolymers
Polytetrafluoroethylene
Polypropylene Fiber
Alkyds and Unsaturated Polyester Resins
Cellulose Nitrate
Polyamides (Nylon 6/12)
Polyester Resins (thermoplastic)
Silicones

Effluent limitations guidelines contained herein set forth the degree of reduction of pollutants in effluents that is attainable through the application of best practicable control technology currently available (BPCTCA), and the degree of reduction attainable through the application of best available technology economically achievable (BATEA) by existing point sources for July 1, 1977, and July 1, 1983, respectively. Standards of performance for new sources are based on the application of best available demonstrated technology (BADT).

Annual costs for this segment of the plastics and synthetics industry for achieving BPCTCA control by 1977 are estimated at $5,000,000, and costs for attaining BATEA control by 1983 are estimated at $12,000,000. The annual cost of BADT for new sources in 1977 is estimated at $3,300,000.

Supporting data and rationale for the development of proposed effluent limitations guidelines and standards of performance are contained in this development document.

Costs, waste and control technology
are [illegible]

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SECTION I

CONCLUSIONS

In this segment of the plastics and synthetics industry, approximately 160 company operations are responsible for the manufacture of products which have been grouped into fifteen product subcategories. Annual production for the fifteen products was estimated to be 1.2 million kkg (2.6 billion lbs) per year or about one-tenth of the volume of the eighteen larger-volume resins surveyed earlier. The volume of effluents currently discharged was estimated to be 90 thousand cu m/day (24 MGD). Water usage (at current hydraulic loads) was projected to increase at 10 percent per year through 1977, while production was projected to increase at 14 percent in the same period.

For the purpose of setting effluent limitations guidelines and standards of performance, the industry parameters giving the most effective categorization were found to be waste water characteristics, specifically, raw waste load, with a BOD$_5$ value of more than or less than 10 kg/kkg of product separating high and low waste load subcategories; and attainable BOD$_5$ concentrations as demonstrated by plastics and synthetics plants using technologies which are defined herein as the basis for BPCTCA. Three groupings were defined with average effluent concentrations under 20 mg/liter (low attainable BOD$_5$ concentration), from 30 to 75 mg/liter (medium attainable BOD$_5$ concentration), and over 75 mg/liter (high attainable BOD$_5$ concentration.

Based on these two dimensions of categorization, four major subcategories were defined.

> Major Subcategory I - low waste load, low attainable BOD$_5$ concentration (4 products: ethylene vinyl acetate, polytetrafluoroethylene, polypropylene fiber, and polyvinylidene chloride).
>
> Major Subcategory II - high waste load, low attainable BOD$_5$ concentration (2 products: acrylic resins and cellulose derivatives).
>
> Major Subcategory III - high or low waste load, medium attainable BOD$_5$ concentration (7 products: alkyd and unsaturated polyester resins, cellulose nitrate, polyamides, saturated thermoplastic polyesters, polyvinyl butyral, polyvinyl ethers,

and silicones).

Major Subcategory IV - high or low waste load, high attainable BOD_5 concentration (2 products: nitrile barrier resins and spandex fibers).

Additional subcategorization within the above four major subcategories was necessary to account for the waste water generation which is specific to individual products and their various processing methods. The separation of each individual product into separate subcategories simplifies the application of the effluent limitations guidelines and standards of performance by providing a clearly defined context for application of the numerical values. The advantages of this double-layered (by waste characteristics and by product) subcategorization appear to outweigh the advantages that might be connected with product group characterization alone.

Annual costs of treatment for the synthetic polymer segment of the plastics and synthetics industry were estimated at $1.8 million. By 1977, under BPCTCA guidelines and assuming full payment of user charges by this industry for municipal treatment, it was estimated that the synthetic polymers industry segment should expect annual costs of $5.0 million - an increase of 23 percent per year. By 1983, under BATEA guidelines, existing plants would be expected to have annual pollution control costs of $12.0 million - an increase of 20 percent per year between 1977 and 1983. By 1977, under BADT-NSPS and projected product growth, the annual costs for new plants are estimated at $3.3 million. The estimated average cost of treatment over the industry for BPCTCA, BATEA, and BADT-NSPS technologies respectively was: $0.16 ($0.63), $0.40 ($1.52), and $0.17 ($0.66) per cubic meter (per thousand gallons).

The average range of water pollution control costs under BPCTCA was estimated at 0.3 to 1.3 percent of current sales price. On average, the range of costs for applying BATEA to existing plants was 0.6 to 3.3 percent of sales price. The cost of BADT-NSPS was estimated at 0.5 percent of sales price over the fifteen product groups.

SECTION II

RECOMMENDATIONS

BOD_5, COD, and total suspended solids and pH are recommended as the critical parameters requiring effluent limitations guidelines and standards. Other pollutant parameters are specific to product subcategories as indicated in the following list. Some of these pollutants are identified as being of potential concern, and others as being ones for which effluent limitations guidelines and standards are recommended.

Subcategory	Pollutant Parameters	Guidelines Recommended
Alkyd compounds and unsaturated polyester resins	lead cobalt	
Polytetrafluoroethylene	fluorides	x
Spandex fibers	cyanides	x
	oils and grease	
	organic nitrogen	
Acrylic resins	oils and grease	
Polypropylene fibers	oils and grease	x
	phosphates	
Nitrile barrier resins	organic nitrogen	
	cyanides	x
Polyamides	organic nitrogen	
Cellulose derivatives	inorganic nitrogen	
Cellulose nitrate	inorganic nitrogen	
Silicones	polychlorinated organics	
	copper	x
	fluorides	
Polyvinylidene chloride	polychlorinated organics	
Polyester resins (thermoplastic)	cobalt manganese cadmium	

Effluent limitations guidelines and standards of performance are proposed for those parameters noted above as based on analogy with other industries, since there were insufficient data available to determine the magnitude of the raw waste loads or their concentration in treated waste waters. However in most cases where metals are used, the combination of neutralization and biological waste water treatment is expected to reduce or remove them to low concentrations which are within the recommended guidelines. In the case of mercury, cyanides, and cadmium the standards for toxic and hazardous chemicals should apply.

Best practicable control technology currently available (BPCTCA) for existing point sources is based on the application of end-of-pipe technology at the production site or the utilization of municipal sewage treatment by facilities with appropriate pretreatment methods. End-of-pipe technologies are considered to be based on biological treatment systems for BOD5 reductions (typified by the activated sludge process, trickling filters, aerated lagoons, aerobic - anaerobic lagoons, and so on). These biological systems are presumed to be preceded by appropriate treatment such as equalization basins to dampen shock loadings, settling, clarification and chemical treatment for removal of solids and adjustment of pH, and subsequent treatment such as clarification or polishing ponds for additional removal of BOD5 and suspended solids. Also, in-plant application of technologies and operational methods which may be helpful in meeting BPCTCA standards include segregation of process contact waste waters from noncontact water, elimination of direct condensers, control of leaks, minimization of housekeeping water usage and establishment of nonwater using housekeeping practices.

Best available technology economically achievable (BATEA) for existing point sources is based on the best in-plant practices of industry which minimizes the generation of waste water pollutants. These are typified by complete segregation of contact process waters from noncontact waste water, maximum recycle and reuse of treated waste water, elimination of all possible contact of water with the processes (for example, by the elimination of barometric condensers), preventing leaking materials from getting into waste water streams, and the application of other methods of removing pollutants (such as the reduction of COD through the use of adsorptive flocs, granular media filtration, chemical treatment, or activated carbon). In some instances, preventing wastes from becoming waterborne results in small volume, highly concentrated streams which can be treated selectively or incinerated.

Best available demonstrated technology (BADT) for New Source Performance Standards (NSPS) is based on BPCTCA technologies and the maximum possible reduction in process waste generation and minimization of waste water flows as outlined for BATEA. The application of granular media filtration and chemical treatment for additional suspended solids and other pollutant removal may be required as well as more than one stage of biological treatment.

The levels of technology considered above as BPCTCA, BATEA, and BADT-NSPS are the bases for effluent limitations guidelines and standards of performance. (Tables II-1, II-2, II-3, II-4, II-5, and II-6). The tables are based upon documented effluent concentrations attained by the techniques outlined above or upon the engineering judgment that available technologies from other industries can be transferred to this one.

Variations in flow rates and the variabilities normally inherent in well designed and operated treatment facilities have been taken into consideration.

TABLE II-1

BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE EFFLUENT LIMITATIONS GUIDELINES [kg/kkg (lb/1000 lb) of production]

Foot-note No.	Subcategory	BOD_5		SUSPENDED SOLIDS	
		Maximum Average of Daily Values for Any Period of Thirty Consecutive Days	Maximum for Any One Day	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days	Maximum for Any One Day
1	Ethylene-Vinyl Acetate Copolymers	0.20	0.39	0.55	1.0
2	Polytetrafluoroethylene	3.6	7.0	9.9	18.0
3	Polypropylene Fiber	0.40	0.78	1.1	2.0
4	Polyvinylidene Chloride	No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote	
5	Acrylic Resins	"	"	"	"
6	Cellulose Derivatives	"	"	"	"
7	Alkyds and Unsaturated Polyester Resins	0.33	0.60	0.22	0.40
8	Cellulose Nitrate	14	26	9.4	17
9	Polyamides (Nylon 6/12 only)	0.66	1.20	0.44	0.80
10	Polyester Resins (thermoplastic)	0.78	1.4	0.52	0.95
11	Polyvinyl Butyral	No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote	
12	Polyvinyl Ethers	"	"	"	"
13	Silicones				
	Fluid	1.0	1.9	0.69	1.25
	Greases, Emulsions, Rubbers, Resins	13.2	24	8.8	16
	Coupling Agents	8.2	15	5.4	10
14	Nitrile Barrier Resins	No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote	
15	Spandex Fibers	"	"	"	"

TABLE II-2

BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE EFFLUENT LIMITATIONS GUIDELINES
(Other Elements and Compounds)

Product	Parameter	kg/kkg (lbs/1000 lbs of production)	
		Maximum average of daily values for any period of thirty consecutive days	Maximum For Any One Day
Alkyds and unsaturated polyester resins			
	Mercury	Toxic and hazardous chemicals guidelines to apply	
Polytetrafluoroethylene	Fluorides	0.6	1.2
Spandex fiber	Cyanides	Toxic and hazardous chemicals guidelines to apply	
Nitrile barrier resins	Cyanides	" " "	" "
Polypropylene fibers	Oils & grease	0.5	1.0
Silicones			
Fluids	Copper	0.005	0.010
Greases, Emulsions, Rubbers and Resins	Copper	0.067	0.13
Coupling Agents	Copper	0.042	0.084
Polyester resins (Thermoplastic)	Cadmium	Toxic and hazardous chemicals guidelines to apply	

TABLE II-3

BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE EFFLUENT LIMITATIONS GUIDELINES
[kg/kkg (lb/1000 lb) of production]

Foot-note No.	Subcategory	BOD_5		COD		SUSPENDED SOLIDS	
		Maximum Average of Daily Values for Any Period of Thirty Consecutive Days	Maximum for Any One Day	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days	Maximum for Any One Day	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days	Maximum for Any One Day
1	Ethylene-Vinyl Acetate Copolymers	0.19	0.29	1.65	2.40	0.14	0.16
2	Polytetrafluoroethylene	2.2	3.3	4.0	5.9	1.6	1.9
3	Polypropylene Fiber	0.22	0.33	0.40	0.59	0.16	0.16
4	Polyvinylidene Chloride	No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote	
5	Acrylic Resins	"	"	"	"	"	"
6	Cellulose Derivatives	"	"	"	"	"	
7	Alkyds and Unsaturated Polyester Resins	0.10	0.14	0.52	0.74	0.03	0.04
8	Cellulose Nitrate	6.9	9.4	34	47	2.1	2.5
9	Polyamides (Nylon 6/12 only)	0.37	0.50	1.9	2.6	0.11	0.12
10	Polyester Resins (thermoplastic)	0.44	0.59	2.3	3.1	0.14	0.16
11	Polyvinyl Butyral	No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote	
12	Polyvinyl Ethers	"	"	"	"	"	"
13	Silicones						
	Fluid	0.37	0.28	3	4	0.21	0.18
	Greases, Emulsions, Rubbers, Resins, and Coupling Agents	6.4	6.8	33.4	45.3	2.0	2.3
14	Nitrile Barrier Resins	No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote	
15	Spandex Fibers	"	"	"	"	"	"

TABLE II-4

BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE EFFLUENT LIMITATIONS GUIDELINES
(Other Elements and Compounds)

Product	Parameter	kg/kkg (lbs/1000 lbs of Production)	
		Maximum average of daily values for any period of thirty consecutive days	Maximum For Any One Day
Alkyds and unsaturated polyester resins	Mercury	Toxic and hazardous chemicals guidelines to apply	
Polytetrafluoroethylene	Fluorides	0.6	1.2
Spandex fibers	Cyanides	Toxic and hazardous chemicals guidelines to apply	
Nitrile barrier resins	Cyanides	" " "	" "
Polypropylene fibers	Oils and grease	0.092	0.18
Silicones			
Fluids	Copper	.0026	.0052
Greases, Emulsions, Rubbers, Resins and Coupling Agents	Copper	.029	.058
Polyester resins (thermoplastic)	Cadmium	Toxic and hazardous chemicals guidelines to apply	

TABLE II-5

BEST AVAILABLE DEMONSTRATED TECHNOLOGY NEW SOURCE PERFORMANCE STANDARDS
[kg/kkg (lb/1000 lb) of production]

		BOD_5		COD		Suspended Solids	
Footnote No.	Subcategory	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days	Maximum for Any One Day	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days	Maximum for Any One Day	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days	Maximum for Any One Day
1	Ethylene-Vinyl Acetate Copolymers	0.18	0.35	1.8	3.5	0.13	0.19
2	Polytetrafluoroethylene	0.80	1.60	1.4	2.9	0.37	0.83
3	Polypropylene Fiber	0.04	0.08	0.07	0.14	0.03	0.04
4	Polyvinylidene Chloride	No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote	
5	Acrylic Resins	"	"	"	"	"	"
6	Cellulose Derivatives	"	"	"	"	"	"
7	Alkyds and Unsaturated Polyester Resins	0.02	0.03	00.11	0.20	0.006	0.008
8	Cellulose Nitrate	6.0	11	30	54	1.8	2.7
	Polyamides (Nylon 6/12 only)	0.37	0.67	1.9	3.4	0.11	0.17
10	Polyester Resins (thermoplastic)	0.44	0.80	6.5	12	0.14	0.20
11	Polyvinyl Butyral						
12	Polyvinyl Ethers	No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote	
13	Silicones						
	Fluid	.57	1.0	4.7	8.5	0.13	0.26
	Greases, Emulsions, Rubbers, Resins, and Coupling Agents	3.5	10	45	82	1.7	2.5
14	Nitrile Barrier Resins	No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote	
15	Spandex Fibers	"	"	"	"	"	"

TABLE II-6

BEST AVAILABLE DEMONSTRATED TECHNOLOGY - NEW SOURCE PERFORMANCE STANDARDS
(Other Elements and Compounds)

Product	Parameter	kg/kkg (lbs/1000 lbs of Production) Maximum average of daily values for any period of thirty consecutive days	kg/kkg (lbs/1000 lbs of Production) Maximum For Any One Day
Alkyds and unsaturated polyester resins			
	Mercury	Toxic and hazardous chemicals guidelines to apply	
Polytetrafluoroethylene	Fluorides	0.6	1.2
Spandex fibers	Cyanides	Toxic and hazardous chemicals guidelines to apply	
Nitrile barrier resins	Cyanides	" " "	" "
Polypropylene fibers	Oils and grease	0.017	0.034
Silicones			
Fluids	Copper	0.0026	0.0052
Greases, Emulsions, Rubbers, Resins and Coupling Agents	Copper	0.025	0.050
Polyester resins (thermoplastic)	Cadmium	Toxic and hazardous chemicals guidelines to apply	

FOOTNOTES FOR TABLES II-1, II-3, II-5

1. Ethylene-Vinyl Acetate (EVA) Copolymer. Two of the five known producers were contacted. All plants are located at polyethylene production facilities. Water use and wastewater characteristics for EVA are essentially identical to those for low density polyethylene. However, an emulsion polymerization process is known and produces a distinctly different waste load which is essentially that of polyvinyl acetate emulsion polymerization reported in EPA 440/1-73/010. Both multi-plant and municipal sewage treatment is used.

2. Polytetrafluoroethylene. Three of the seven manufacturing plants were visited. A wide range of products are produced. The most important is polytetrafluoroethylene (PTFE) and these guidelines are recommended for PTFE granular and fine powder grades only. The wastewater discharges differ considerably depending upon the process recovery schemes for hydrochloric acid and the disposal of selected streams by deep well, ocean dumping or off-site contract methods. The use of ethylene glycol in a process can significantly affect the waste loads. Fluoride concentrations in untreated wastewaters are generally below levels attainable by alkaline precipitation.

3. Polypropylene Fibers. Two of the three producers were contacted. The volumetric flow ranges per unit of production vary widely depending upon the type of cooling system used. The waste loads are for plants where selected concentrated wastes are segragated and disposed of by landfilling, etc. Primary treatment at one plant site was observed while the other plant discharges to a municipal sewage system.

4. Polyvinylidene Chloride. The two major manufacturers were contacted. Both plant sites send wastewaters to multi-plant treatment plants of which the polyvinylidene chloride is a small portion. Consequently, there was insufficient data to develop recommended guidelines.

5. Acrylic Resins. Three of the four manufacturers were contacted. Large numbers of product grades are produced by bulk, solution, suspension and emulsion polymerization. The widely varying hydraulic loads for the large number of products in addition to treatment of the wastewaters by multi-plant wastewater treatment facilities prohibited obtaining sufficient meaningful data to recommend effluent limitation guidelines.

6. Cellulose Derivatives. Cellulose derivates investigated included ethyl cellulose, hydroxyethyl cellulose, methyl cellulose and carboxymethyl cellulose. Wide variations in unit flow rates for two plants producing the same product, differences in manufacturing techniques and the availability of data prevented recommending guidelines. The wastewaters from the three manufacturers are being treated in multi-plant wastewater treatment facilities or will enter municipal sewage systems.

7. Alkyds and Unsaturated Polyester Resins. Six carefully selected plants were visited to provide a cross-section of the industry for size of operation, type of manufacturing process and wastewater treatment methods. Hydraulic loads vary widely depending upon the process designs. Similarly, raw waste loads vary widely because some plants segragate wastes for disposal in other manners. Generally, the industry discharges wastewaters into municipal sewage systems and should continue. Also, the type of air pollution control, e.g. combustion or scrubbing, has a significant effect on the wastewater loads. The recommended guidelines are for plants having their own wastewater treatment system - a very infrequent occurrence.

8. Cellulose Nitrate. The two major manufacturers of the four manufacturers were contacted. These wastes require pH control and contain large amounts of nitrates. One plant discharges to a municipal sewage system while the other goes into a multi-plant treatment complex.

9. Polyamides. Various polyamides are produced but only Nylon 6/12 produces significant amounts of wastewater, e.g. Nylon 11 uses no process water. Consequently, the guidelines are restricted to Nylon 6/12 and were developed on the basis of similarity with waste loads from Nylon 66 production.

10. Polyester Thermoplastic Resins. There are three manufacturers, two of which produce poly(ethylene, terephthalate) in quantities less than 2% of their total thermoplastic production. The guidelines are recommended for poly(ethylene terephthalate) since the other product poly(butylene terephthalate) is produced at only one plant and the wastewater goes into a municipal sewage system, so no data on performance could be obtained.

11. Polyvinyl Butyral. Of three production sites, two have processes beginning with vinyl-acetate monomer which generates much larger wastewater volumes than the process beginning with polyvinyl alcohol. Since the manufacturing sites where production starts with a monomer discharge into municipal sewage systems, there was no data available. Consequently, there are no recommended guidelines since they would be tantamount to establishing a permit for the direct discharger production site.

12. Polyvinyl ethers. The three present plants use different processes each of which produces several grades of product. The different chemical compositions used in both bulk and solution polymerization processes and the lack of data on both raw and treated wastewaters prevented establishing guidelines. The wastewaters are presently sent to either multi-plant treatment facilitis or municipal sewage systems.

13. Silicones. Four companies manufacture silicones at five locations. Three plants were visited and data were obtained from all plants. The major processing steps at the five plants are shown below.

Major Processes at Five Silicone Plants

Plant No.	1	2	3	4	5
CH_3Cl	x		x	x	
Chlorosilane prod.	x	x	x	x	x
Hydrolysis	x	x	x	x	x
Fluids, greases, emulsions prod.	x	x	x	x	x
Resin production	x	x	x		
Elastomer production	x	x	x		x
Specialties prod.*	x	x	x		
Fumed silica prod.			x		
HCl production					x

* e.g. surfactants, fluorinated silicones, coupling agents, and other materials.

Based on the manufacturing process, the waste water flows and the raw waste loads, the plants 1, 2, 3 and 5 were designated as multi-product plants while 4 was designated as a fluid product plant.

14. Nitrile Barrier Resins. Commercial scale production and sale of these resins has not yet begun. The companies expected to have production facilities were contacted, and two provided estimates of raw waste loads. Because of the lack of demonstrated flows and raw waste loads, it was impossible to establish effluent guideline limitations.

~~15.~~ Spandex Fibers. Three manufacturers each produce Spandex fibers by significantly different processes. These are dry, wet and reaction spinning methods. Because of limited data on raw waste loads and because each plant operates a different process, it was impossible to establish meaningful guidelines.

SECTION III

INTRODUCTION

Purpose and Authority

Section 301(b) of the Act requires the achievement by not later than July 1, 1977, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best practicable control technology currently available as defined by the Administrator pursuant to Section 304(b) of the Act. Section 301(b) also requires the achievement by not later than July 1, 1983, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best available technology economically achievable which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants, as determined in accordance with regulations issued by the Administrator pursuant to Section 305(b) of the Act. Section 306 of the Act requires achievement by new sources of a Federal standard of performance providing for the control of the discharge of pollutants which reflects the greatest degree of effluent reduction which the Administrator determines to be achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives, including, where practicable, a standard permitting no discharge of pollutants.

Section 304(b) of the Act requires the Administrator to publish within one year of enactment of the Act, regulations providing guidelines for effluent limitations setting forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the degree of effluent reduction attainable through the application of the best control measures and procedure innovations, operation methods and other alternatives. The regulations proposed herein set forth effluent limitations guidelines pursuant to Section 304(b) of the Act for the lower volume products of the plastics and synthetic materials manufacturing source category.

Section 306 of the Act requires the Administrator, within one year after a category of sources is included in a list published pursuant to Section 306(b) (1) (A) of the Act, to propose regulations establishing Federal standards of performances for new sources within such categories. The

Administrator published in the Federal Register on January 16, 1973 (38 F.R. 1624), a list of 27 source categories. Publication of the list constituted announcement of the Administrator's intention of establishing, under Section 306, standards of performance applicable to new sources within the plastic and synthetic materials manufacturing source category, which was included within the list published January 16, 1973.

Methodology

The effluent limitations guidelines and standards of performance proposed herein were developed in the following manner for this second group of specialty plastics and synthetics that are generally produced in smaller volumes than the first group.

Because establishing guideline limitations for one or two plants would be tantamount to prescribing the limitations for the plants' discharge permit and because plants with less than one million pounds per year of production are nearly always installed at multi-product facilities, it was decided to include only those products being produced at three or more plants in quantities of at least one million pounds per year. The products were examined for categorization on the basis of raw material, products, manufacturing processes, raw waste characteristics, and the demonstration or availability of waste water treatment technology.

The raw waste characteristics for each subcategory were identified through analyses of (1) the sources and volumes of water and waste waters emitted from the processing plants and (2) the thermal conditions and pollutants including toxic or hazardous substances and other constituents which might result in taste, odor, or color problems or toxicity to aquatic organism. The constituents within each subcategory which should be subject to effluent limitations guidelines and standards of performance were identified from information on process operating conditions and data on waste water analyses.

The types of waste water control and treatment technologies existing in the industry were identified. This includes an identification of each distinct control and treatment technology for both in-process and end-of-process technologies which are existent or capable of being engineered for each subcategory. It also includes an identification of the pollutants in terms of chemical, physical, and biological characteristics, and the effluent concentration levels resulting from the application of each of the treatment and control technologies. The problems, limitations, and reliability of each treatment control technology were also identified as well as the time required for implementation. In addition, certain other nonwater environmental impacts were discussed, such as the effects of control technologies on other pollution problem areas (e.g., air, solid wastes, noise, and radioactivity). Energy demand requirements for each of the control and treatment technologies were developed, and the cost of applying such technology was estimated.

The information outlined above was then evaluated to determine what levels of waste water treatment technologies constituted the "best practicable control technology currently available (BPCTCA)," the "best available technology economically achievable (BATEA)," and the "best available demonstrated control technology, processes, operating methods, or other alternatives." In identifying such technologies, various factors were considered. These include the total cost of applying the technology in relation to the age of both the equipment and the facility involved, the processes employed, the engineering aspects of applying various types of control techniques through process changes, nonwater quality environmental impact (including energy requirements), the treatability of waste water, water use practices, and other factors.

The data for identification of industry segments, analyses of waste water generation rates, evaluation of process control technology and determination of waste water treatment technologies were developed from a number of sources. These sources included public information from the U.S. EPA research and development efforts, data from permits filed under the 1899 Refuse Act permit program, records of selected state agencies, published literature, surveys of waste water treatment practices by the Manufacturing Chemists Association and by EPA contractors, qualified technical consultants, interviews with industry personnel, and on-site inspection of manufacturing processes and waste water treatment facilities. References used in developing guidelines for effluent limitations and standards of performance of new sources reported here for this segment of the plastics and synthetics industry are essentially the same as those reported in EPA 440/1-73/010 (16) and are listed in Section XIII of this document. Because this segment of the industry represents generally less well known and smaller volume products, significant amounts of information on manufacturing processes were obtained from the companies and are included in files developed to support this Development Document.

General Description of the Industry

The plastics and synthetics industry is composed of three separate segments: the manufacture of the raw materials or monomers, the conversion of these monomers into a resin plastic material, and the conversion of the plastic materials into products such as toys, synthetic fiber, packaging film, adhesives, and so on. The development document for the first group of plastics and synthetics (EPA 440/1-73/010a) was concerned primarily with the manufacture of the basic plastic or synthetic resins (SIC 2821); however, also included were the production of synthetic fibers such as nylon (SIC 2824), man-made fibers such as rayon (SIC 2823), and cellulose film or cellophane (SIC 3074). The first industry grouping dealt with 16 of the major resins, most of the major synthetic fibers, and all of the cellulose fibers and cellophane film, that is, over 90 percent of the total volume of the industry. Consequently, this group of plastics and synthetic products deals with the remaining less than 10 percent of the industry. The large number of products (45) encompassed in this segment of the industry is indicated in Table III-1, which lists the plastics and synthetics fibers to be considered in the second phase of the work on development of effluent limitations guidelines and new source performance standards.

The total production of this segment of the industry is approximately 1.2 million kkg (2.6 billion lbs) of which approximately 0.7 million kkg (1.5 billion lbs) is accounted for in the production of unsaturated polyesters by over 40 producers. The remaining products are generally produced by less than four manufacturers. Because many of the products are manufactured to end use specifications, it is not possible to categorize the industry commercially except in a very general way, such as price range, size product, size of market, or potential growth. From a commercial point of view, this segment of the synthetics and plastics industry can be divided into four generally distinct groups. The first group is the relatively new, high performance, low volume and high priced materials, e.g., selling generally at over $6.60/kg ($3.00/lb), such as chlorinated polyethers, methyl pentene, phenoxy resins, parylene phosphonitrilic resins, polyaryl ether, polybenzothiazoles, polyethylene amines, polybenzimidazoles, polyimides, polymethylpentene, polyphenylene sulfide, poly alpha-methyl styrene, and polyvinyl carbazol. A second group is the older materials which have a significant market and, being medium priced, are generally produced by a limited number of companies. These are the cellulosics, polyvinyl butyral, diallyl phthalates, polytetrafluoroethylene, silicones, pyrrolidines, and vinylidene chloride. A relatively new and fast growing third group encompasses ionomers, nitrile barrier resins, polyphenylene oxide, and polybutenes. The fourth group is those relatively large volume resins which can anticipate good growth such as methacrylates, polyesters, polycarbonates, and ethylene-vinyl acetate.

TABLE III-1

PLASTICS AND SYNTHETICS FOR CONSIDERATION

Alkyd Molding Compounds
Amine Resins
Cellulose Acetate Butyrate
Cellulose Acetate Propionate
Cellulose Butyrate
Cellulose Nitrate
Cellulose Propionate
Chlorinated Polyethers
Chlorinated Polyethylene
Diallyl Phthalate Compounds
DuPont Nitrile Barrier Resins (NR-16)
Ethyl Cellulose
Ethylene-Vinyl Acetate
Fluorocarbons
    CTFE (Kel-F) Chlorotrifluoroethylene
    FEP
    TFE - Teflon Polytetrafluoroethylene
    PVDF - Polyvinyldifluoride
Ionomers, Acrylics - Surlyn
LOPAC (Monsanto) + BAREX (Sohio) (Nitrile Barrier Resin)
Methyl Cellulose
Parylene (U.C.)
Phenoxy Resins
Phosphonitrilic Resins
Polyallomer (PE/PP Copolymer)
Poly-alpha-methyl Styrene
Polyamides
Polyaryl Ether (Arylon)
Polybenzimidazoles
Polybenzothiazoles
Polybutene
Polycarbonate
Polyethylene Imines
Polymethacrylonitrile Resins
Polymethylacrylate
Polymethyl Pentene (ICI's TPX)
Polyphenylene Oxides (Noryl)
Polyphenylene Sulfide (Ryton-Phillips)
Polypropylene Fibers
Polysulfones
Polyvinyl Butyral
Polyvinyl Carbazoles
Polyvinyl Ethers
Polyvinyl Pyrrolidone
Silicones
Unsaturated Polyesters

The basis for selecting products from this segment of the industry for the development of effluent limitations guidelines was set as follows: at least 454 kg (1 million lbs) of the material must be produced at a single manufacturing site, and three or more manufacturers must produce the material. These criteria were chosen because location or production facilities for lesser quantities would be very difficult to establish, and developing guidelines for products manufactured in only one or two plants would be tantamount to writing the permits under the National Pollution Discharge Elimination System for the one or two plants, which is not within the scope of this work. With these prerequisites, an extensive survey of the following literature sources was made to determine names and numbers of manufacturers, and production rates.

> Chemical Economics Handbook, Stanford Research Institute.
>
> Directory of Chemical Producers, 1973, USA, Chemical Information Services, S.R.K.
>
> Modern Plastics Encyclopedia, 1972-1973, Suppliers-Resins and Molding Compounds.
>
> Plastics World, 1972-1973, Directory of the Plastics Industry.
>
> Chemical Horizons File, Predicast, including updates to July 1973 (this includes references to journals such as Chemical Week).
>
> Chemical Marketing Reporter, "Chemical Profile" Section, from June 26, 1972, through July 23, 1973.

An exhaustive review of this information indicated it was often impossible to delineate between basic producers and distributors of compounds or products, and many discrepancies were found in reported production capacities. Consequently, the literature sources were supplemented with information from both the contractor's files and direct contact with companies in order to establish that there were three or more plants producing a specific product or that there were two or less producers. In those product categories where only two producers were listed in the original searches, the companies were contacted to ascertain whether or not there were other producers. Where only three producers were found originally, we contacted any companies we were uncertain of to confirm that they were indeed basic producers and not distributors. Products selected for the development of effluent limitations guidelines are listed in Table III-2. These include 13 from the original list of Table III-1 plus the following three additional products, which were found to meet the selection criteria and which were not considered in the Phase I work of this contract or by other EPA contractors:

Polyamides (other than Nylon 6 and 66)

Thermoplastic polyesters

Spandex fibers

Therefore, 29 products were eliminated between the two lists. The principal reasons for elimination of these 29 products are summarized below.

1.	Misnomer or duplicates	4
2.	Families of compounds or further generic groupings	5
3.	Insufficient number of production sites	20
	TOTAL ELIMINATED	29

A short discussion of the rationale for eliminating the nine products in categories (1) and (2) above follows.

(1) Misnomers or duplicates

Amine resins - not a meaningful designation for a specific or generic group of products.

Cellulose butyrate - not an article of commerce - probably meant to apply to cellulose acetate butyrate.

Polymethacrylonitrile resins - combined with the more general category of nitrile barrier resins.

Methyl pentene - another name for polymethyl pentene.

(2) Families of compounds or further generic groupings.

The product category "cellulose derivatives" was created by combining methyl cellulose, ethyl cellulose, cellulose propionate, cellulose acetate propionate, and cellulose acetate butyrate from the original list plus two additional materials, hydroxymethyl cellulose and carboxy methyl cellulose (CMC). This category was established because the total production of these cellulose derivatives was judged to be important for the development of effluent limitations guidelines, although none of the individual products is made by more than two companies. These products are regrouped below into general processes and the specific products are shown.

TABLE III-2

PRODUCTS TO BE CONSIDERED FOR DEVELOPMENT OF EFFLUENT GUIDELINE LIMITATIONS

Acrylic resins
Alkyd molding compounds
Cellulose derivatives
Cellulose nitrate
Ethylene-vinyl acetate copolymers
Nitrile barrier resins
Polyamides (other than Nylon 6 and 66)
Polyester resins (thermoplastic)
Polyester resins (unsaturated)
Polypropylene fibers
Polytetrafluoroethylene
Polyvinyl butyral
Polyvinyl ethers
Polyvinylidene chloride and copolymers
Silicones
Spandex fibers

Derivative

Alkali Processes

(a) methyl cellulose,
(b) ethyl cellulose,
(c) carbomethyl cellulose,
(d) hydroxyethyl cellulose

Acid Processes

(e) cellulose acetate butyrate,
(f) cellulose acetate propionate,
(g) cellulose propionate

Items (a) through (d) are made by dissolving cellulose in alkali and reacting with CH_3Cl, C_2H_5Cl, $ClCH_2COOH$ or $\underset{O}{C-C}$ respectively NaCl being in most cases the biggest by-product. The esters (e) through (f) are synthesized in acid medium, rather than alkali, using acetic, propionic and/or butyric acids.

Nitrile barrier resins were chosen as the generic grouping for the following products:

DuPont's NR-16 (R)

Monsanto's Lopac (R)

Sohio's Barex (R)

Although these products are only produced in limited quantities at the present time, they are believed to be potentially large volume products.

(3) Insufficient number of production sites.

The remaining 20 products were eliminated from consideration because no more than two manufacturing plants could be found or because they are manufactured in less than one million pounds per year quantities at a plant. The products are listed in Table III-3.

TABLE III-3

PRODUCTS ELIMINATED FROM CONSIDERATION FOR ESTABLISHMENT OF EFFLUENT GUIDELINE LIMITATIONS

Product
Chlorinated Polyethers
Chlorinated Polyethylene
Diallyl Phthalate Compounds
Ionomers
Parylene
Phenoxy Resins
Phosphonitrilic Resins
Polyallomer
Poly-alpha-Methyl Styrene
Polyaryl Ethers
Polybenzimidazoles
Polybenzothiazoles
Polybutylene (called polybutene in Table I)
Polycarbonates
Polyethylene Imine
Polymethyl Pentene
Polyphenylene Oxides
Polysulfone
Polyvinyl Carbazole
Polyvinyl Pyrrolidone
Urethane Prepolymers

In addition, three of the original product names were changed, i.e., (1) polybutenes are more correctly listed as polybutylenes (in the plastics and synthetics field polybutenes are tars whereas polybutylene is a specific isomer of polybutylene used in film and pipe formation), (2) poly(vinyl and vinylidene) chloride was reinterpreted to mean polyvinylidene chloride since effluent limitations guidelines for polyvinyl chloride were developed in the Phase I study, and (3) polymethyl methacrylate was placed into the more generic category "acrylic resins."

Those companies which were determined to be manufacturers (not suppliers or distributors only) of the products selected for consideration in the development of effluent limitations guidelines are shown in Table III-4.

Product and Process Technology

Brief descriptions of the chemical nature of the products and the manufacturing process technology are presented in this section with special emphasis on indicating those process operations which generate waste waters. These descriptions are presented in alphabetical order for the products regardless of whether guidelines are established or not. In some instances the only available information was from patents and the literature since manufacturing processes remain proprietary; in some instances no information was available.

TABLE III-4

MANUFACTURERS OF PRODUCTS TO BE CONSIDERED FOR DEVELOPMENT OF EFFLUENT LIMITATION GUIDELINES

	Dow	Dow Corning	Celanese	duPont	Monsanto	Sohio	Allied Chemical	Ameliotex, Inc.	ICI	Globe	Pennwalt	Union Carbide	Air Products	Hercules	Cheveron	Phillips	BASF Wyandotte	GAF	Grace	Vulcan	Ashland	General Electric	PPG	Reichhold	Westinghouse	Aquitaine Organic	Cyanamid	Rohm & Haas	SWS Silicones (Stauffer)	Swedlow	Chemplex	Tennessee Eastman
Cellulose Nitrate				x										x																		
Nitrile Barrier Resins				x	x	x																										
Fluorocarbon Polymers				x			x		x		x																					
Ethylene-Vinyl Acetate	x			x			x					x	x				x														x	
Polypropylene Fibers														x	x	x																
Polyvinyl Butyral				x	x							x																				
Polyvinyl Ethers												x					x	x														
Polyvinylidene Chloride	x																		x	x												
Alkyd Molding Compounds			x				x													x	x				x							
Polyester Resins (Unsat.)							x												x				x	x								
Polyester Resins (Thermoplastic)			x																			x										x
Acrylic Resins				x								x															x	x		x		
Silicones		x										x										x							x			
Polyamides (Except Nylon 6 and 66)				x	x							x														x						
Cellulose Derivatives	x											x		x																		x
Spandex Fibers								x		x				x																		

Acrylic Resins

Polymers have been produced commercially from a wide variety of different esters of both acrylic acid and methacrylic acid. Specialty plastics have been produced from 2-haloacrylic esters and 2-cyanoacrylic esters. In recent years the production of methacrylate polymers has exceeded production of acrylic polymers. Since production methods are similar, methyl methacrylate polymers will be discussed here as representative of the acrylate resins.

Methacrylic acid, $CH_2C(CH_3)COOH$, can be considered as the parent substance from which methyl methacrylate monomer and poly(methyl methacrylate) and all other methacrylate compounds are derived. In one process, methyl methacrylate monomer is manufactured starting with acetone cyanohydrin and 98 percent sulfuric acid. The methacrylamide sulfate formed as an intermediate is not isolated but reacts with methanol to produce methyl methacrylate. Both steps are carried out continuously. The reaction sequence is shown in Figure III-1, Equation 1.

Polymerization of methyl methacrylate produces poly(methyl methacrylate). The clarity, outstanding weather resistance, light weight, formability, and strength of poly(methyl methacrylate) have led to extensive use of acrylic plastics in aircraft glazing, signs, lighting, construction, transportation, appliances, and merchandising. Because of excellent suspending, rheological, and durability characteristics, acrylic emulsions have wide use in paints for exterior and interior applications on wood, masonry, metals, etc.

Manufacture - Monomer is delivered to the polymerization manufacturer usually in tank car quantities. Low concentration (5-15 ppm) of inhibitor is often adequate for safe handling and storage of methyl methacrylate. Low inhibitor content is desirable, since subsequent polymerization without first removing the inhibitor is possible.

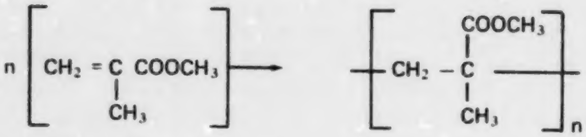
The polymerization of methyl methacrylate shown in Figure III-1, Equation 2, may be conducted in a variety of ways. In commercial casting of sheets of poly(methyl methacrylate) each sheet is cast in a mold assembled from two sheets of plate glass spaced apart at the edges by a gasket (see Figure III-2). The mold is filled by pouring in a charge of monomer with exact amounts of catalyst, colorant if desired, or other additives for special effects. The closed mold then goes through a controlled temperature cycle, generally

(1)

$$(CH_3)_2C(OH)(CN) + H_2SO_4 \longrightarrow CH_2 = C(CH_2)CONH_2 \bullet H_2SO_4$$

$$CH_2 = C(CH_2)CONH_2 \bullet H_2SO_4 + CH_2OH \longrightarrow CH_2 = C(CH_2)COOCH_3 + NH_4HSO_4$$

(2)



$$n\left[\begin{array}{c}CH_2 = \underset{\underset{CH_3}{|}}{C}\ COOCH_3\end{array}\right] \longrightarrow \left[\begin{array}{c} CH_2 - \overset{\overset{COOCH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} \end{array}\right]_n$$

(where n is 500 to 3000)

FIGURE III–1 TYPICAL REACTIONS TO FORM POLY (METHYL METHACRYLATE) – INCLUDING MONOMER MANUFACTURE

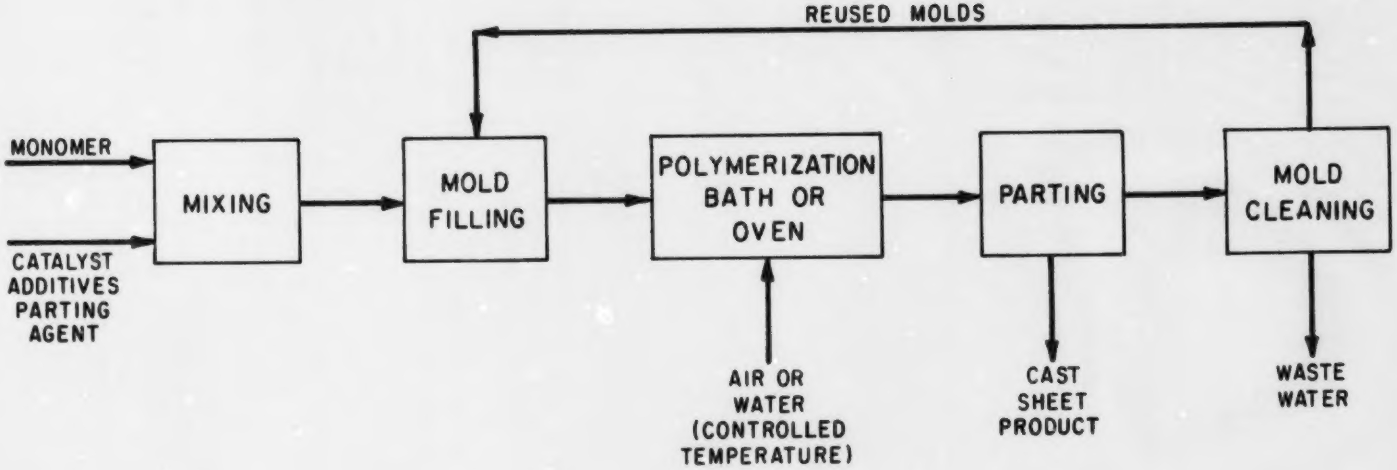

REUSED MOLDS
MONOMER
CATALYST ADDITIVES PARTING AGENT
MIXING
MOLD FILLING
POLYMERIZATION BATH OR OVEN
PARTING
MOLD CLEANING
AIR OR WATER (CONTROLLED TEMPERATURE)
CAST SHEET PRODUCT
WASTE WATER

FIGURE III-2 ACRYLIC RESIN PRODUCTION – BULK POLYMERIZATION PROCESS

between 40 and 75°C (113 and 158°F). Annealing often follows the casting process.

Homo- and copolymers can also be conveniently prepared by an emulsion technique. In a representative procedure shown in Figure III-3, methyl methacrylate is emulsified with an anionic emulsifier and deionized water containing a little ferrous sulfate and ammonium peroxysulfate. The emulsion is flushed with nitrogen and then treated at 20°C (68°F) with small quantities of sodium metabisulfite and t-butyl hydroperoxide. The temperature rises spontaneously to 70°C (158°F) and the polymerization is completed at this temperature in about 15 minutes. After the batch is cooled to room temperature, the product typically contains 35 percent total solids with a viscosity of about 6 cp and a pH of 2.5.

In suspension as well as in emulsion polymerization, water is used as a heat transfer medium in the reaction zone, but the methods differ in the state in which the polymer is obtained. Suspension polymerization (see Figure III-4) yields discrete beads, granules, or particles ranging in size from a few microns to a fraction of an inch in diameter.

With water as the reaction medium, the following factors have to be controlled for successful suspension polymerization methods:

1. The initiator should be soluble in the monomer and insoluble in water. This prevents the polymerization from occurring in the aqueous phase and is especially necessary when the monomer is appreciably soluble in water.

2. Suspending agents may be used to prevent droplet contact and merging and to aid in the suspension of polymerizing droplets. Such agents may be soluble products such as cellulose derivatives, starches, gums, and salts of acrylic polymers; polyvinyl alcohol, or they may be insoluble materials such as clay or talc. Thickeners such as polyoxyalkylene derivatives may also be present to prevent droplet contact.

3. Inorganic salts are often added to increase the density of the aqueous medium, to reduce the water solubility of the monomers, and to increase the interfacial tension of the system.

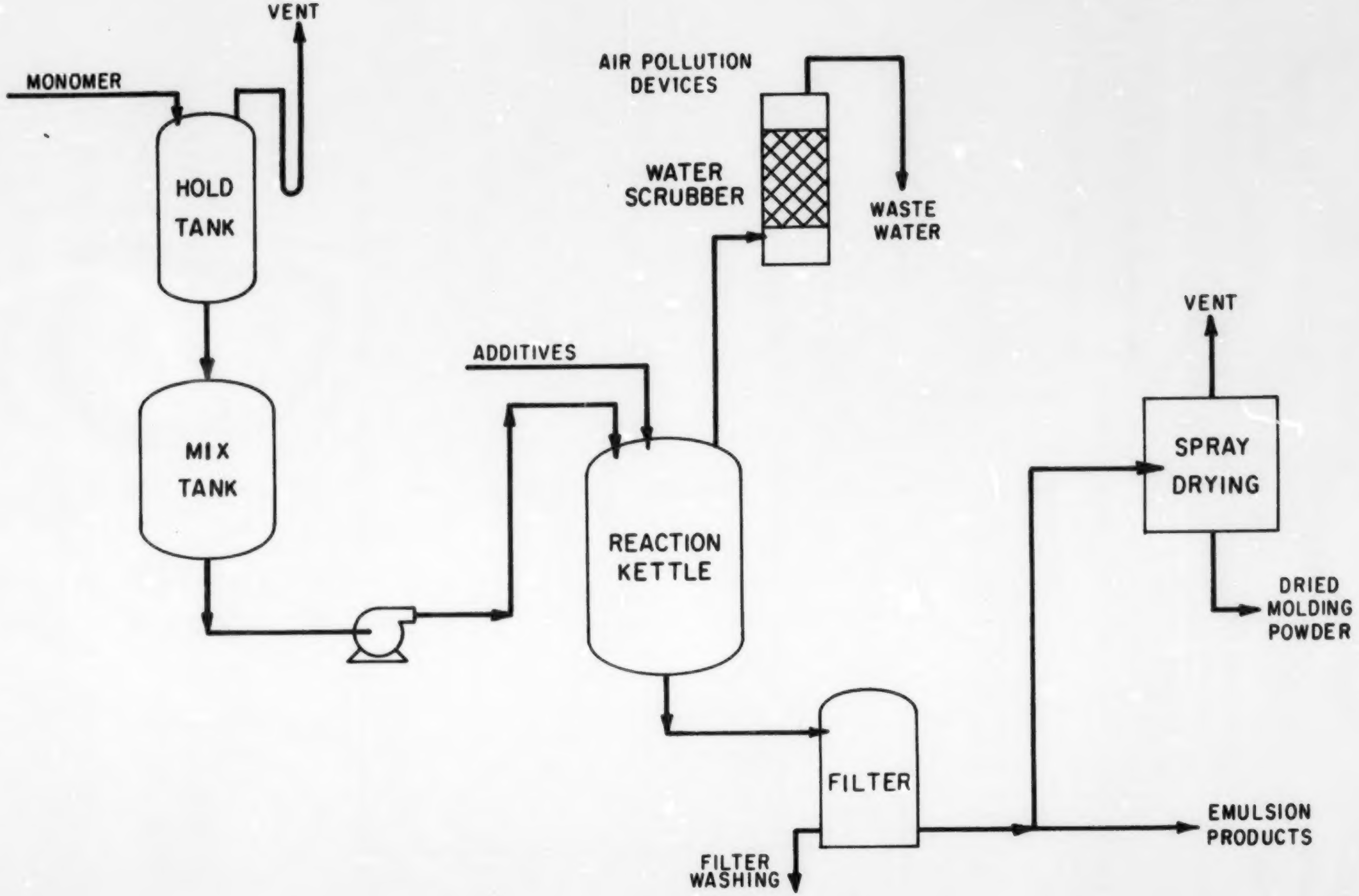
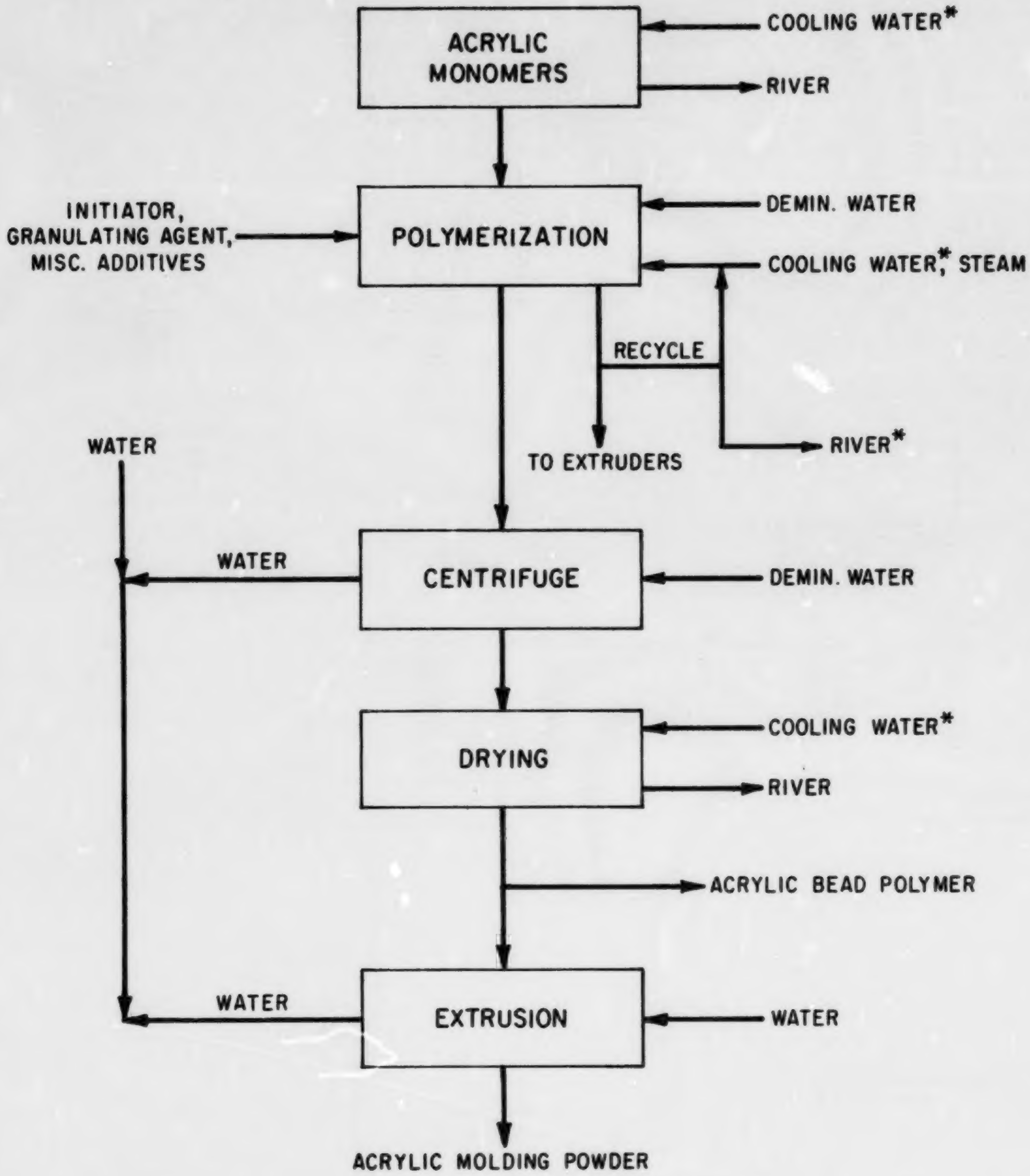

VENT
MONOMER
HOLD TANK
MIX TANK
ADDITIVES
AIR POLLUTION DEVICES
WATER SCRUBBER
WASTE WATER
REACTION KETTLE
VENT
SPRAY DRYING
DRIED MOLDING POWDER
FILTER
FILTER WASHING
EMULSION PRODUCTS

FIGURE III-3 ACRYLIC RESIN PRODUCTION – EMULSION POLYMERIZATION PROCESS


ACRYLIC MONOMERS
COOLING WATER*
RIVER
INITIATOR, GRANULATING AGENT, MISC. ADDITIVES
POLYMERIZATION
DEMIN. WATER
COOLING WATER,* STEAM
RECYCLE
TO EXTRUDERS
RIVER*
WATER
WATER
CENTRIFUGE
DEMIN. WATER
DRYING
COOLING WATER*
RIVER
ACRYLIC BEAD POLYMER
WATER
EXTRUSION
WATER
ACRYLIC MOLDING POWDER

* NON-CONTACT WATER

FIGURE III-4 ACRYLIC RESIN PRODUCTION – SUSPENSION POLYMERIZATION PROCESS

Waste Water Generation - The primary waste water streams are obvious from inspection of the process schematic diagram. Upon cooling, the polymer product is washed, usually within the cooling vessel, and the water or brine leaving this vessel will be contaminated with some monomer, some polymer, and the various stabilizing, emulsifying, and chain-regulating agents as well as the catalyst. Final dewatering occurs in the centrifuge, and the waste water stream from this equipment will contain the same type of contaminants listed above.

If the monomer is assumed to be present at its saturation concentration in the wash water, it will comprise approximately 1.5 percent in the waste stream. If two volumes of water per volume polymer are used to wash the product beads, then 1335 mass units of water will be released per 1000 mass units of polymer product (spec. gr. = 1.5).

There is no water of reaction for the polymerization of methyl methacrylate (25).

Other Pollutants

Oil and grease are due to the presence of lubricants used for the extrusion process. Depending on the specific waste water chemical conditions and the analytical methods used, cyanides may be detected due to the presence of cyanoacrylic esters and acetone cyanohydrin.

Alkyd Molding Compounds

Alkyd molding compounds are mixtures of unsaturated polyester or polyalkyd resins with various fillers and additives which are incorporated to obtain the specific physical characteristics required for the compression molding of parts. The terms alkyd and polyester are often used interchangeably, and indeed alkyds are chemically very similar to unsaturated polyesters (see Unsaturated Polyester Resin section of this report). The primary difference is that in alkyds the acid component is supplied by long chain unsaturated acids rather than the phthalic and maleic anhydrides which are used in unsaturated polyesters. The primary use of alkyd resins is for paint formulations, but they are also used in molding compounds. The alkyds used for paints are often made in the same plant as unsaturated polyesters. When used for paints, the alkyds are diluted with the appropriate paint solvent and sold as a liquid in drums. In this form they contain no monomeric reactive diluent.

Manufacture - Alkyd molding compounds are sold in the form of free flowing powder, gunk, and pastes. They are usually prepared in two steps. The resin producer carries out the polymerization and sometimes adds a reactive diluent, such as diallyl phthalate or styrene, and sells the resin to a compounder in liquid form. The compounder then adds the appropriate fillers such as glass, fiber, asbestos, clay, calcium carbonate or alumina, and packages the alkyd molding compound in a form appropriate to be sold to a molder. The process description and guidelines developed for the resin manufacturer should be applicable to the manufacture of the liquid alkyd resins which are used to make molding compounds as well as for alkyds for paints (which are not covered by this study) and unsaturated polyester resin manufacture.

Waste Water Generation - Waste water production in the polymerization process is similar to that described in the section on Polyester Resins. The compounding steps are all mechanical and do not generate liquid waste (41).

Cellulose Derivatives

This group of materials includes ethyl cellulose, methyl cellulose, carboxymethyl cellulose, and hydroxyethyl cellulose. All are ethers of cellulose.

The first three of these derivatives are made by reaction of an alkyl chloride -- ethyl chloride, methyl chloride, and chloracetic acid -- with cellulose. Hydroxyethyl cellulose is made by reaction of ethylene oxide with cellulose. Several of the commercial grades of methyl cellulose are mixed ethers, made by reaction of propylene oxide as well as methyl chloride with cellulose. Equations (1) through (4) in Figure III-5 express the general reactions involved.

All of the reactions are run using alkali cellulose -- a mixture of cellulose with sodium hydroxide. In the course of the reactions involving alkyl halides ±(1), (2), (3)1, the alkali is neutralized by formation of sodium chloride. This salt, and excess alkali, must be removed from some of the products to provide materials that are usable.

Manufacture - Figure III-6 on the following page shows a block flow diagram for production of cellulose ethers. The use of a solvent in the process maintains the cellulose as a relatively easy-to-handle slurry. Depending on the cellulose derivative involved, the solvent may be either an alcohol or a hydrocarbon.

Proprietary processes appear to be widely used in production of cellulose ethers. Manufacturers refuse to discuss the processes in any detail.

Uses of the cellulose ethers are varied. Ethyl cellulose is a plastic. Methyl cellulose, carboxymethyl cellulose, and hydroxyethyl cellulose are water soluble and are generally used in applications involving water solubility. Carboxymethyl cellulose may be used as a suspending agent. Methyl cellulose is used as a film former. All three ethers are used in certain foodstuffs.

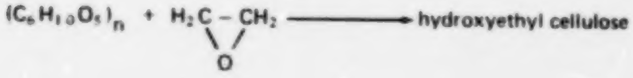
Waste Water Generation - Wastes generated in production of cellulose derivatives constitute alkali, salt, solvent residues, pulp, and treatment chemicals. These wastes indicate relatively high BOD, COD, and dissolved solids levels (41). Organic nitrogen may be present in the waste waters of facilities where nitrogen containing cellulose derivatives (other than cellulose nitrate) are produced.

(1) $(C_6H_{10}O_5)_n + CH_3Cl + NaOH \longrightarrow \text{methyl cellulose} + NaCl + H_2O$

(2) $(C_6H_{10}O_5)_n + C_2H_5Cl + NaOH \longrightarrow \text{ethyl cellulose} + NaCl + H_2O$

(3) $(C_6H_{10}O_5)_n + ClC_2H_3O_2Na + NaOH \longrightarrow \text{carboxymethyl cellulose} + NaCl + H_2O$

(4)



$(C_6H_{10}O_5)_n + \underset{\diagdown\ \diagup \atop O}{H_2C - CH_2} \longrightarrow \text{hydroxyethyl cellulose}$

FIGURE III–5 TYPICAL REACTIONS TO FORM CELLULOSE DERIVATIVES

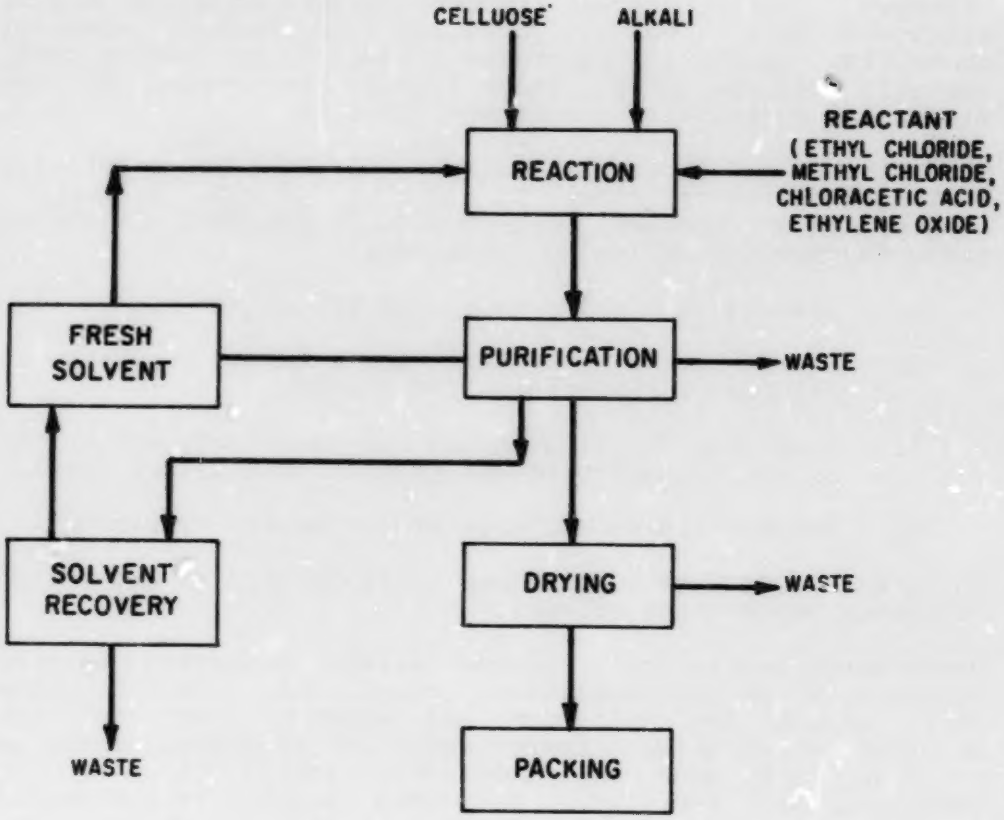

CELLULOSE
ALKALI
REACTANT
(ETHYL CHLORIDE,
METHYL CHLORIDE,
CHLORACETIC ACID,
ETHYLENE OXIDE)
REACTION
FRESH SOLVENT
PURIFICATION
WASTE
SOLVENT RECOVERY
DRYING
WASTE
WASTE
PACKING

FIGURE III-6 CELLULOSE ETHERS PRODUCTION

Cellulose Nitrate

Cellulose nitrate is produced by reaction of fibrous cellulose with a mixture of nitric and sulfuric acids. The equation of reaction is shown in Figure III-7.

Manufacture - From the equation in Figure III-7 one may calculate that cellulose nitrate contains 14.1 percent nitrogen. The commercial product contains about 12 percent nitrogen; this level is attained by using mixtures containing carefully controlled amounts of nitric acid, sulfuric acid and water. These liquids are present in the mix in the approximate proportion 1:3:0.75.

The fibrous nature of the original cellulose is essentially unaltered by the reaction. In order to provide a commercially useful product, the initially obtained nitrate is taken through the following processes:

1. Washing with water to remove all acid.
2. Stabilization by boiling with water to remove small amounts of combined sulfuric acid.
3. Digestion (heating in the presence of water) to reduce viscosity of the product to a useful level.
4. Dehydration or exchange of the water, by alcohol.

The steps listed above are shown in Figure III-8, which also indicates waste water streams.

Waste Water Generation - Aqueous wastes generated in the manufacture of nitrocellulose constitute primarily acids (both nitric and sulfuric) and alcohol lost in the dehydration process. Spent acids are recovered as far as possible, but some are inevitably lost. Alcohol is recovered and recycled. Suspended solids in the wastes include a small amount of cellulosic material. The strongly acidic wastes are handled by neutralization with lime. The calcium sulfate which is formed may be removed by settling (41).

$$(C_6H_{10}O_5)_n + 3\,HNO_3 + H_2SO_4 \rightleftharpoons (C_6H_7O_2\,(NO_3)_3)_n + H_2O + H_2SO_4$$

FIGURE III–7 TYPICAL REACTION TO FORM CELLULOSE NITRATE

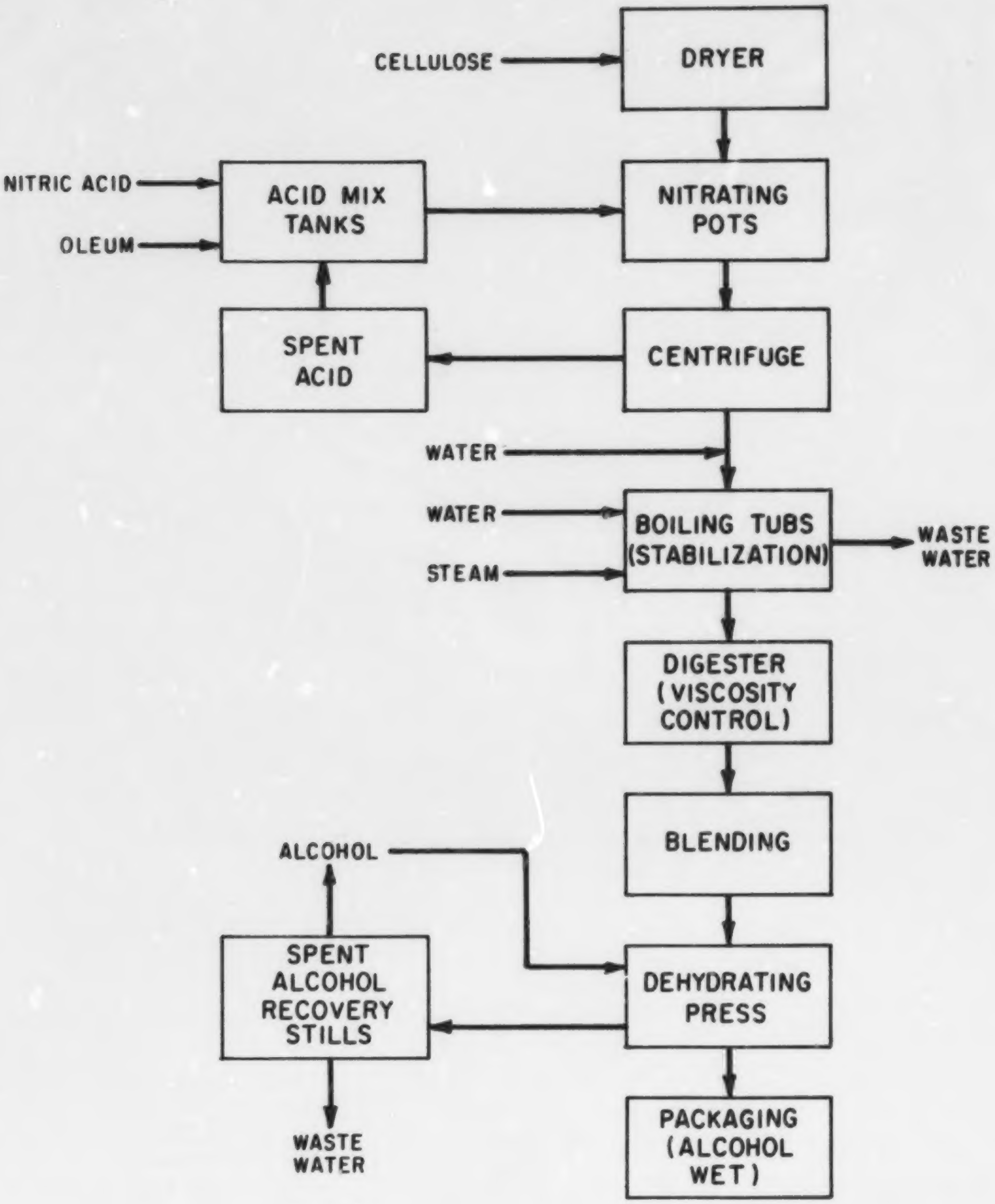

CELLULOSE
DRYER
NITRIC ACID
OLEUM
ACID MIX TANKS
NITRATING POTS
SPENT ACID
CENTRIFUGE
WATER
WATER
STEAM
BOILING TUBS (STABILIZATION)
WASTE WATER
DIGESTER (VISCOSITY CONTROL)
BLENDING
ALCOHOL
SPENT ALCOHOL RECOVERY STILLS
DEHYDRATING PRESS
WASTE WATER
PACKAGING (ALCOHOL WET)

FIGURE III-8 CELLULOSE NITRATE PRODUCTION

Chlorinated Polyethylene

Polyethylene may be chlorinated either in solution or more commonly as a suspension in an inert diluent such as water, acetic acid, or cold carbon tetrachloride. When water is used, reaction temperatures between 50-65°C (122-149°F) are used, and a suitable catalyst is necessary to establish economic reaction rates at atmospheric pressure. Artificial light of wavelength below 4785 A and certain azo compounds are effective for accelerating the reaction. No catalyst is needed, however, at reaction temperatures when pressures are greater than 7 atmospheres (100 psig) or greater. The reaction equation is given in Figure III-9.

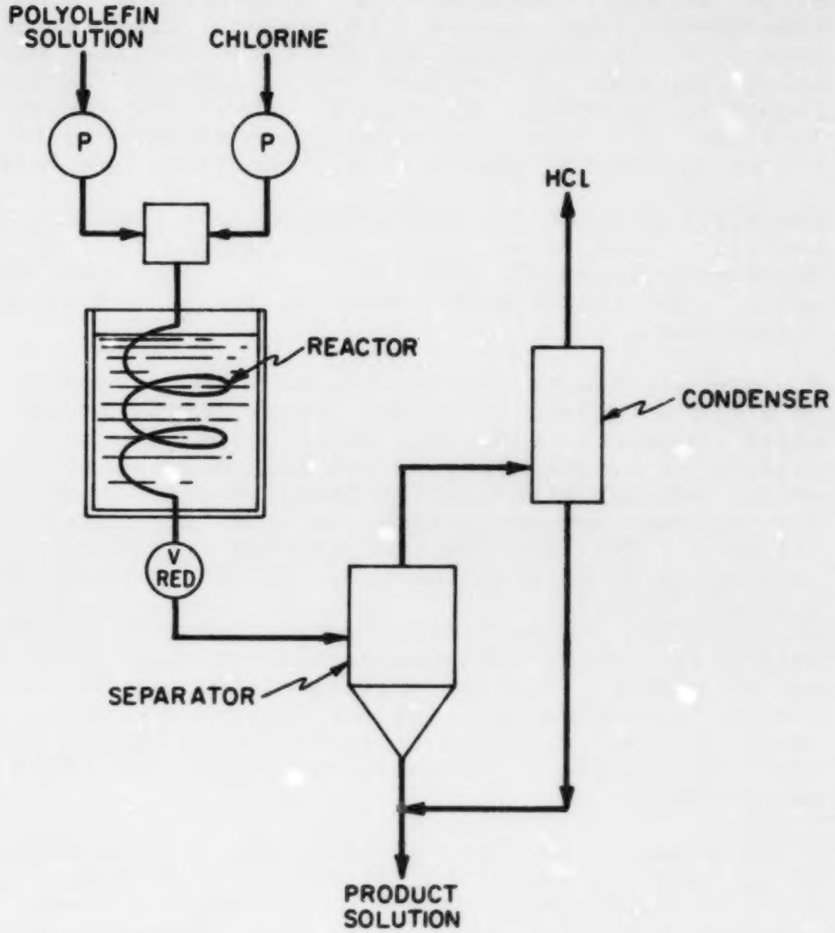
The chlorinated polyethylenes are currently used commercially to improve the impact strength and processibility of polyvinylchloride, as an elastomer having good chemical resistance, as a blending agent with PVC in the manufacture of floor tile, and as a blending agent in other multi-component plastic compositions.

Manufacture - A flow chart for a typical chlorination is shown in Figure III-10. Feed materials are polyethylene in hot carbon tetrachloride solution and chlorine. These are fed into a liquid phase tubular reactor. The reaction temperature is between 50-150°C (122-302°F) at pressures as high as 20 atmospheres (300 psig). The reaction time for the exothermic reaction is about 5 minutes (44). After reaction, the polymerized product is separated from HCl, a by-product of the reaction.

Waste Generation - The primary waste generated is the by-product hydrogen chloride. Recovery or other disposal of hydrogen chloride (or hydrochloric acid vapor or solution) would be the primary environmental concern. About 590 mass units of HCl (dry basis) would be generated per 1000 mass units of product (5, 10, 11, 40, 44, 45).

$$-\!\!\left[CH_2 - CH_2 \right]\!\!-_n + Cl_2 \longrightarrow -\!\!\left[CHCl - CH_2 \right]\!\!-_n + HCl$$

FIGURE III-9 TYPICAL REACTION TO FORM CHLORINATED POLYETHYLENE


POLYOLEFIN SOLUTION
CHLORINE
P
P
HCL
REACTOR
CONDENSER
V RED
SEPARATOR
PRODUCT SOLUTION

FEED MATERIALS	kg/1000 kg PRODUCT
POLYETHYLENE	450
CHLORINE	1140

SOURCE: U.S. PATENT 2,964,509 BY D.M. HURT (TO DU PONT)
(DECEMBER 13, 1960).

FIGURE III-10 CHLORINATED POLYETHYLENE PRODUCTION

Diallyl Phthalate Resins

Diallyl phthalate was one of the earliest unsaturated polyester resins. It is a member of the allyl family of resins. The basis for this family of resins is allyl alcohol (Figure III-11, Equation 1). The vinyl group in the allyl alcohol provides the unsaturation through which subsequent free radical initiated crosslinking or chain extension can take place in order to cure the resin. When allyl alcohol is reacted with phthalic anhydride, the resulting product is diallyl phthalate (Figure III-11, Equation 2). This product is manufactured in the United States by the FMC Corporation, Princeton, New Jersey.

The allyl alcohol can be condensed with either the orthophthalic anhydride to produce diallyl orthophthalate (trademark Dapon 35, FMC Corp.) or with the isophthalate acid. The isophthalate ester is identified as Dapon M, FMC Corporation.

The product can be used as either a low viscosity monomer or as a higher molecular weight thermoplastic prepolymer. The allyl monomers and, in some cases, the prepolymers find utility as crosslinking agents for other unsaturated polyester resins, either in conjunction with or as a substitute for styrene monomer which is the conventional reactive diluent. The low vapor pressure at molding temperatures (2.4 mm of mercury at 149°C or 300°F) favors the use of diallyl phthalate over styrene, particularly for larger parts. This low volatility permits allylic polyesters to be molded at higher temperatures than styrene polyester, and, as a result, faster molding cycles can be achieved (30). Another advantage of using the allylic monomers or prepolymers as the reactive diluent in unsaturated polyesters is that they result in formulations with lower volume shrinkage on curing.

A major use of the diallyl phthalate compounds when used by themselves is critical electrical/electronic applications which require a high degree of reliability under long-term, adverse environmental conditions. Examples are electrical connectors used in communications, computer, aerospace, and other systems, as well as insulators, potentiometers, and circuit boards.

Diallyl phthalate prepolymer is also used as a surfacing medium for decorative laminates and in combination with polyester resin systems to meet the growing demand for economical, low pressure laminates.

(1) $CH_2 = CH - CH_2 - OH$

(2)

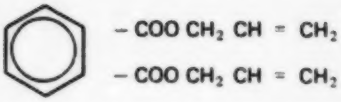

– COO CH₂ CH = CH₂
– COO CH₂ CH = CH₂

FIGURE III–11 TYPICAL REACTIONS TO FORM DIALLYL PHTHALATE

Manufacture - Conventional polycondensation batch reactor type technology is used to form the diallyl phthalate. Conventional free radical methods are used in extending the molecular weight of the monomeric diallyl phthalate (30).

Ethylene-Vinyl Acetate Copolymers

Manufacture - Ethylene-vinyl acetate (EVA) copolymers with vinyl acetate contents in the range of about 7-40 percent by weight are manufactured in the same facilities as low density polyethylene (LDPE) and often with high density polyethylene (HDPE). A process flow diagram is shown in Figure III-12. The same equipment is used for EVA copolymers as for LDPE except for additional facilities needed for recovery of unreacted vinyl acetate and ethylene. This equipment consists of a separator downstream from the polymerization autoclave, where the solid EVA particles are sent to the pelletizing operation and the liquid phase is distilled to recover ethylene and vinyl acetate. The distillate wastes consist of a waxy residue that is incinerated or used as fuel.

In the overall process, shown in Figure III-12, vinyl acetate and ethylene monomers are fed to a compressor to build up the pressure necessary for polymerization. Polymerization is carried out in an autoclave using a peroxide type initiator. Following polymerization, the pressure is reduced and the mixture of unreacted vinyl acetate and ethylene, together with EVA copolymer, is sent to a separator. The separated EVA copolymer is fed to an extruder (where residual ethylene gas is removed and returned to the compressor) which extrudes continuous strands into a water chill bath where they are mechanically cut into pellets. The polymer pellets are screened from the water and spin dried.

The liquid phase from the separator is distilled for recovery of monomers, and the final residue incinerated as described above.

As the final process step, the EVA pellets are remelted, combined with additives and repelletized. Examples of additives are diatomaceous earth, amides, butylated hydroxy toluene, and various cyclic organic compounds. Since many of the end uses for the product involve direct contact with foods, it is produced to meet FDA requirements.

An EVA copolymer with distinctly different characteristics from those described above is produced by an emulsion polymerization process. The emulsion copolymer has a very high vinyl acetate content. It is made at only one plant, which is unrelated to those plants using the LDPE process. The emulsion polymerization process and associated waste water loads are essentially the same as those reported for poly-

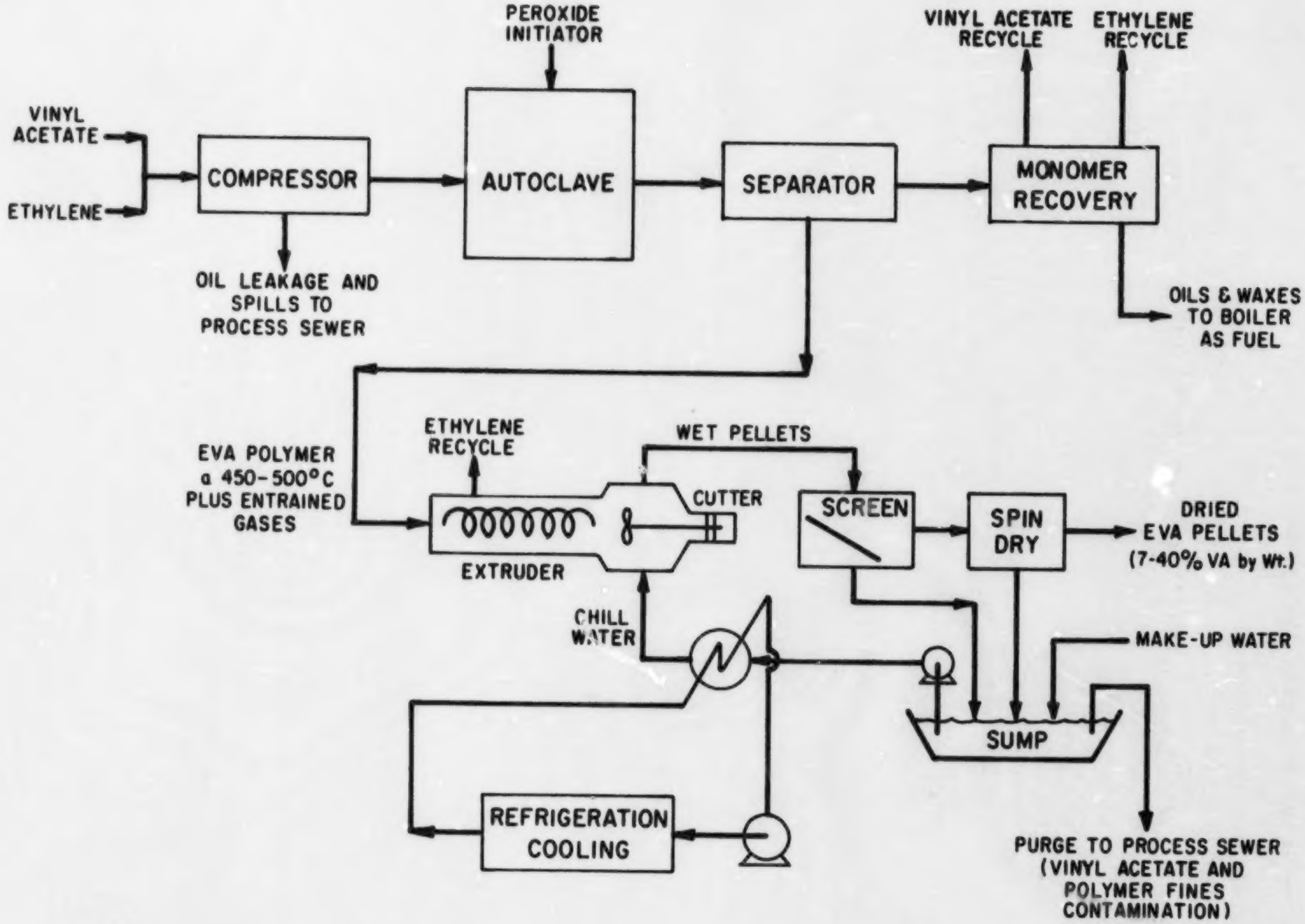

PEROXIDE INITIATOR
VINYL ACETATE RECYCLE
ETHYLENE RECYCLE
VINYL ACETATE
ETHYLENE
COMPRESSOR
AUTOCLAVE
SEPARATOR
MONOMER RECOVERY
OIL LEAKAGE AND SPILLS TO PROCESS SEWER
OILS & WAXES TO BOILER AS FUEL
ETHYLENE RECYCLE
WET PELLETS
EVA POLYMER a 450-500°C PLUS ENTRAINED GASES
CUTTER
SCREEN
SPIN DRY
DRIED EVA PELLETS (7-40% VA by Wt.)
EXTRUDER
CHILL WATER
MAKE-UP WATER
SUMP
REFRIGERATION COOLING
PURGE TO PROCESS SEWER (VINYL ACETATE AND POLYMER FINES CONTAMINATION)

FIGURE III-12 ETHYLENE-VINYL ACETATE COPOLYMER PRODUCTION

vinyl acetate homopolymer emulsion in EPA Development Document No. EPA 440/1-73/010 (61).

Waste Water Generation - In plants using LDPE equipment for EVA production, the pelletizer cooling water is generally recirculated through the refrigeration cooling system. A continuous purge is maintained to control vinyl acetate and polymer fines contamination in the recirculated water. Vinyl acetate which enters the waste waters from the purge stream is biodegradable both as the intact compound and in the form of its hydrolysis products, acetaldehyde, and acetic acid.

Other waste sources are oil leakage and spills from compressors and pumps which enter area surface water drainage ditches. Washdown water from processing and loading areas also flows to the drainage ditches and is another source of vinyl acetate contamination. The waste stream from the ditches is skimmed to recover oil and EVA particles. The oil is incinerated and the EVA is either land-filled or sold to scrap reprocessors (16, 25).

Fluorocarbon Polymers

The term "fluorocarbon polymers" as used in this report refers to addition type polymers in which all, or a significant portion, of the substituent groups on the carbon atoms in the polymer chain are fluorine. Typically, the balance of the substituents are chlorine and/or hydrogen. The fluorocarbon polymer family encompasses a range of homopolymer, copolymer, and terpolymer compositions as indicated by the list shown in Table III-5. Most of the products are in the plastics category, but elastomer grade polymers have also been included.

Polytetrafluoroethylene (PTFE) is by far the most important commercial polymer in this group and accounts for an estimated 75 percent or more of the total production. PTFE is produced in two dry product forms (granular and fine powder) and as an aqueous dispersion. It is the only fluorocarbon polymer produced in three different plants. In view of the relative significance of PTFE, the process descriptions below have been divided to separate PTFE from the other fluorocarbon polymers.

Practice varies widely from plant to plant in this industry. Some plants produce only one type; more commonly several types of fluorocarbon polymers are made at the same plant. However, since most of the polymers are proprietary, the product mix differs from plant to plant. All existing plants are located within larger chemical complexes. The practice with respect to production of monomer and monomer feedstock varies. TFE monomer is produced on-site in all cases. Production of other monomers and monomer feedstocks (chlorodifluoromethane in the case of TFE) may or may not be carried out at the same plant. From examination of available waste load data related to production of the various polymers and in view of the widely varying practices from plant to plant, we have concluded that waste water guidelines should be limited to the dominant products - granular and fine powder grades of PTFE - and that aqueous dispersion grade and all other fluorocarbon polymers must be considered as unique products.

It is also characteristic of this industry that process technology is considered highly confidential. The process descriptions that follow, therefore, are necessarily general in nature.

A. Polytetrafluoroethylene (PTFE)

1. TFE Monomer Process

Since TFE monomer is produced on-site in all cases, we have included monomer synthesis as part of the overall polymer process.

Manufacture - TFE monomer is produced by continuous process based on pyrolysis of chlorodifluromethane (Refrigerant 22) as indicated by the flowsheet shown in Figure III-13. The main reaction involved is shown at the top of Figure III-14. Various other fluorinated side products may also be formed in minor amounts.

The process stream from the reaction furnace is scrubbed first with water, then with dilute caustic solution to remove by-product HCl and other soluble components. After the caustic scrub, the gas stream is dried either with concentrated sulfuric acid or with ethylene glycol. The dry gas stream is compressed and distilled to recover purified TFE monomer. Extremely pure monomer is required for subsequent polymerization.

Waste Water Generation - The sources of waste water generation from the TFE monomer process are indicated in Figure III-13. The effluent from the water scrubber is a dilute solution of HCl. This stream is the only significant source of fluoride discharge from the process. In general, waste waters from TFE monomer and polymer processes do not contain appreciable amounts of fluoride. (However, greater amounts of fluoride are generated in the production of the monomer precursor, Refrigerant 22.) The effluent from the caustic scrubbers contains very dilute caustic and dissolved salts. In those cases where sulfuric acid is used for drying the gas stream, strong acid solution is recovered from the drying tower. Where ethylene glycol is used for the drying step, a small amount of glycol is lost in the glycol recycle operation and contributes a minor BOD load in the waste water stream.

2. PTFE Polymerization

Manufacture - Polymerization of TFE to the homopolymer, PTFE, proceeds by free-radical addition polymerization typical of olefins. The polymerization is carried out under pressure in aqueous media in batch reactors. The literature suggests initiators such as sodium or potassium peroxydisulfates may be employed. The polymerization reaction is indicated in Figure III-14 and a generalized flowsheet of the process is shown in Figure III-15.

PTFE is produced for sale in several forms: a granular or pellet form, a fine powder, and aqueous dispersion. The dry

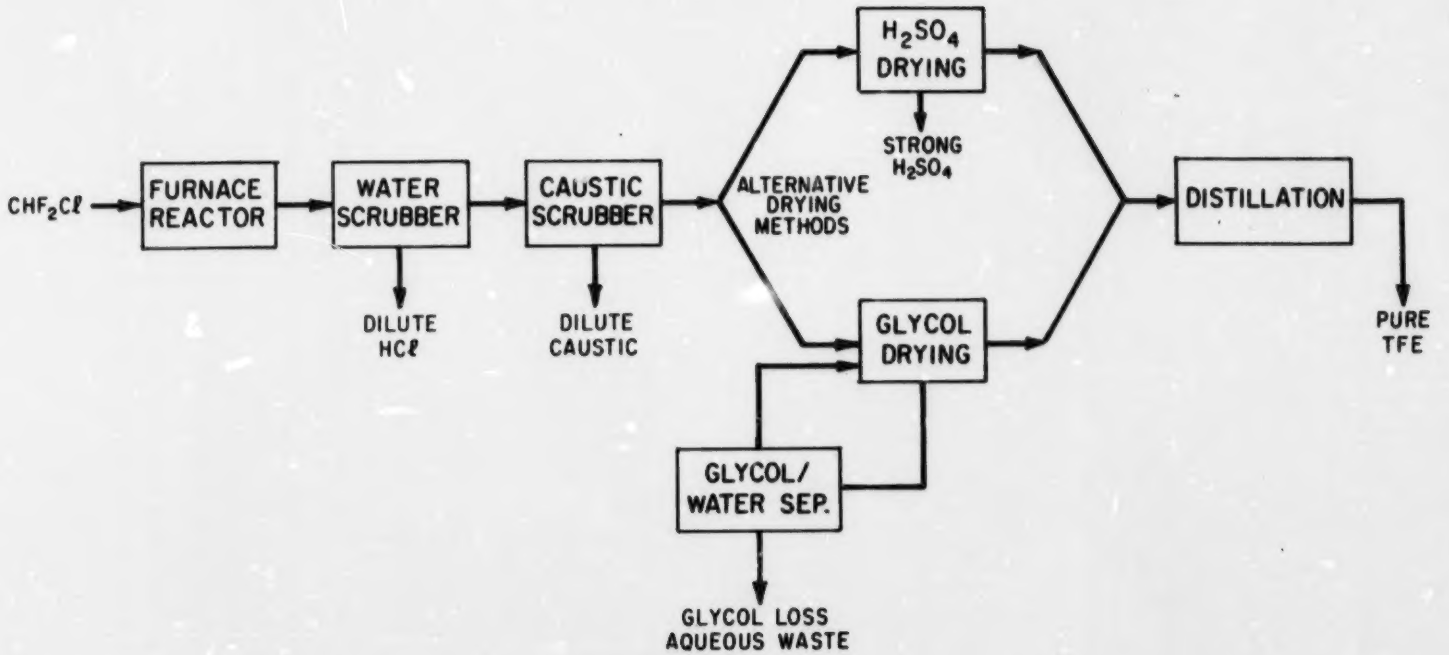
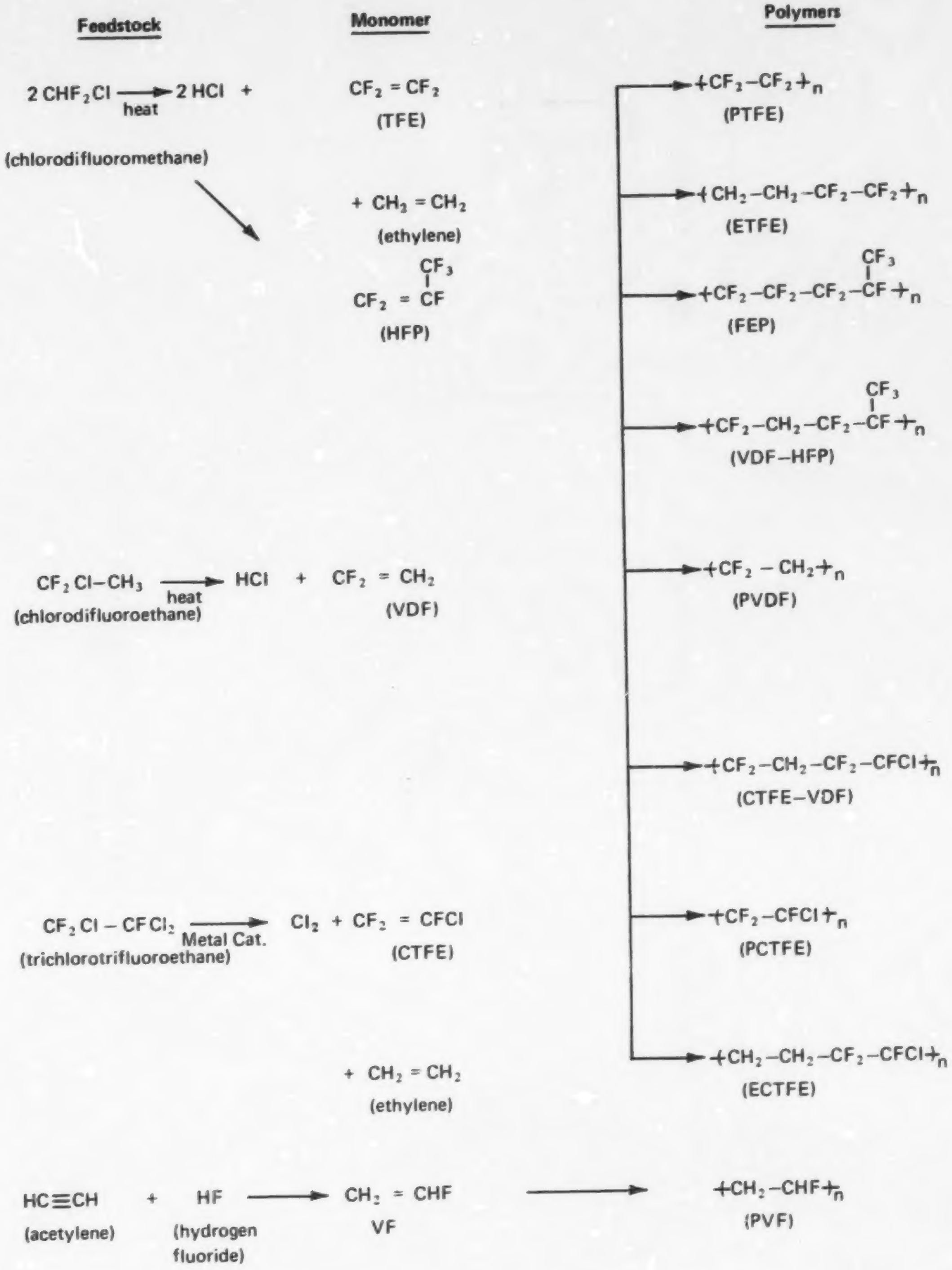

CHF_2Cl
FURNACE REACTOR
WATER SCRUBBER
DILUTE HCl
CAUSTIC SCRUBBER
DILUTE CAUSTIC
ALTERNATIVE DRYING METHODS
H_2SO_4 DRYING
STRONG H_2SO_4
GLYCOL DRYING
GLYCOL/ WATER SEP.
GLYCOL LOSS AQUEOUS WASTE
DISTILLATION
PURE TFE

FIGURE III-13 POLYTETRAFLUOROETHYLENE (PTFE) PRODUCTION — TFE MONOMER PROCESS


Feedstock
Monomer
Polymers
2 CHF₂Cl → 2 HCl + (heat)
CF₂ = CF₂
(TFE)
(chlorodifluoromethane)
+ CH₂ = CH₂
(ethylene)
CF₂ = CF–CF₃
(HFP)
CF₂Cl–CH₃ → HCl + CF₂ = CH₂ (heat)
(chlorodifluoroethane)
(VDF)
CF₂Cl – CFCl₂ → Cl₂ + CF₂ = CFCl (Metal Cat.)
(trichlorotrifluoroethane)
(CTFE)
+ CH₂ = CH₂
(ethylene)
HC≡CH + HF → CH₂ = CHF
(acetylene)
(hydrogen fluoride)
VF
–(CF₂–CF₂)–n
(PTFE)
–(CH₂–CH₂–CF₂–CF₂)–n
(ETFE)
–(CF₂–CF₂–CF₂–CF(CF₃))–n
(FEP)
–(CF₂–CH₂–CF₂–CF(CF₃))–n
(VDF–HFP)
–(CF₂ – CH₂)–n
(PVDF)
–(CF₂–CH₂–CF₂–CFCl)–n
(CTFE–VDF)
–(CF₂–CFCl)–n
(PCTFE)
–(CH₂–CH₂–CF₂–CFCl)–n
(ECTFE)
–(CH₂–CHF)–n
(PVF)

Source: *Chemical Economics Handbook*, Stanford Research Institute.

FIGURE III–14 TYPICAL REACTIONS TO FORM FLUOROCARBON POLYMERS

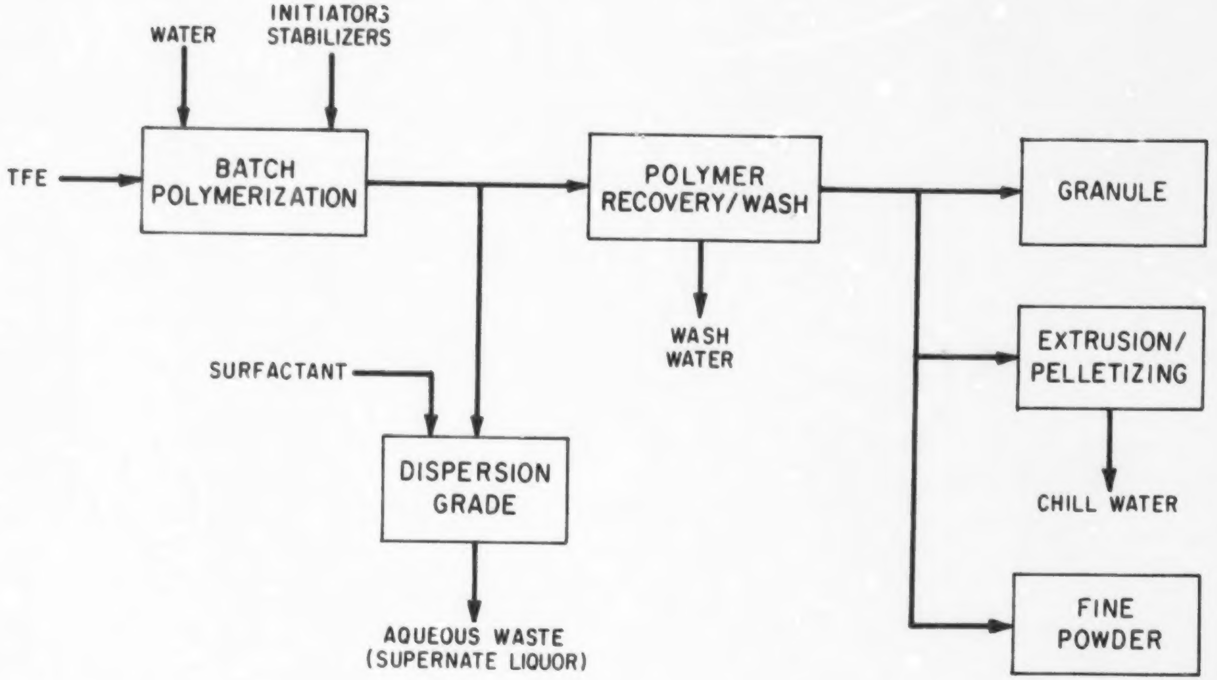

WATER
INITIATORS STABILIZERS
TFE
BATCH POLYMERIZATION
POLYMER RECOVERY/WASH
GRANULE
WASH WATER
EXTRUSION/ PELLETIZING
SURFACTANT
DISPERSION GRADE
CHILL WATER
FINE POWDER
AQUEOUS WASTE (SUPERNATE LIQUOR)

FIGURE III-15 POLYTETRAFLUOROETHYLENE (PTFE) PRODUCTION – PTFE POLYMER PROCESS

product forms, granular and fine powder, account for the major portion of PTFE production. Guidelines have been proposed for these dry product forms only. Dispersion grade is made by only two of the three plants presently producing PTFE.

Waste water Generation - Water is used as the polymerization medium in producing all forms of PTFE, but subsequent process water use and waste water discharge varies with the form being produced. High purity, demineralized process water is required in all cases.

For granular or pellet grades, process water use in addition to polymerization medium includes polymer wash water and, for pellets, chill water for extrusion/pelletizing operations. The process water discharged from these operations is very clean. In one plant, all the process water is collected and recycled through a purification system. In the production of fine powder grade PTFE, wash water is required to purify the polymer particles. The conditions required to produce fine powder grade are such that the water discharged from the polymerization and washing steps may contain a higher level of suspended and dissolved solids than in the case of granular product.

In the production of the dispersion form of PTFE, the polymerization batch is concentrated after addition of a surfactant to stabilize the dispersion. The supernate liquor from the concentrating step is discharged as a waste stream. This stream has a BOD load due to presence of the surfactant.

B. Other Fluorocarbon Polymers

The nature of other fluorocarbon polymers produced is indicated by the list presented in Table III-5. Since most of these polymers are proprietary and process technology is considered highly confidential, it is not possible to give detailed process descriptions. Reactions taken from the literature, indicating the routes to most of these polymers, are given in Figure III-14.

The polymerization step is comparable to that used for PTFE in that the polymerization is carried out in aqueous (purified water) medium in batch kettles. Subsequent steps may vary significantly with the type of polymer and form of product made. These steps may include concentration and stabilization of a dispersion form of the product; filtration or coagulation to recover polymer particles; polymer washing with water or solvent; conversion to final product form by drying granules or powder, extrusion of pellet or film forms, or solvent casting. Recovery operations to recover organic solvents or other proprietary additives may also be associated with some of the polymer processes (6, 29, 30).

TABLE III-5

COMMERCIAL FLUOROCARBON POLYMERS

Polymer	Abbreviation
Polytetrafluoroethylene	PTFE
Fluorinated Ethylene - Propylene	FEP
Poly(ethylene - tetrafluoroethylene)	ETFE
Chlorotrifluoroethylene	CTFE
Poly(ethylene - chlorotrifluoroethylene)	ECTFE
Poly(chlorotrifluorothylene - vinylidene fluoride)	CTFE-VDF
Polyvinyl Fluoride	PVF
Polyvinylidene Fluoride	PVDF
Poly(vinylidene fluoride - hexafluoropropylene)	VDF-HFP

Nitrile Barrier Resins

This class of resins has assumed importance primarily because nitrile barrier resins are transparent polymers with good resistance to passage of gases and solvents. They are in the early stages of being utilized for beverage containers. The nitrile group is the source of these good barrier properties. The nitrile group originates from the presence of either acrylonitrile or methacrylonitrile in the final polymeric structure. The nitrile content was previously restricted to below 30 percent in order to produce resins with acceptable processibility. At this level, the barrier properties were not exceptional. Recent developments have been in the direction of producing resins which have higher nitrile content while still retaining adequate processibility by conventional thermoplastic methods (i.e., extrusion, injection molding, blow molding, thermoforming).

The exact details of resin composition are considered proprietary by the resin manufacturers. The general structure however may be viewed as a butadiene backbone to which acrylonitrile/ methylacrylate or acrylonitrile/styrene copolymers are attached by grafting.

The exact nature of the technical developments which have resulted in this breakthrough is closely held proprietary knowledge by the three U.S. resin suppliers competing in this field.

Any of the generally known polymerization methods (such as bulk, solution, or emulsion) could be used to prepare these resins. Emulsion polymerization is undoubtedly the preferred method. The final composition may result from a two-step polymerization scheme in which a copolymer (such as acrylonitrile/acrylate) is polymerized by emulsion techniques in the presence of a previously formed graft copolymer (such as acrylonitrile/ butadiene).

The polymerization scheme described below is speculative and is based on a review of in-house information and published literature. It is believed, however, that it is a reasonable representation of a typical polymerization process.

A typical polymerization procedure would involve a two-step process in which the acrylonitrile butadiene graft copolymer is made by batchwise emulsion polymerization of a recipe such as that listed below (48).

Typical Latex Recipe	Parts
Acrylonitrile	40
1,3-butadiene	60
Emulsifier	2.4
Azodiisobutyronitrile	0.3
t-dodecyl mercaptan	0.5
Water	200

Before starting the reaction, pH is adjusted to about 8 using potassium hydroxide. Conversion of 92 percent can be obtained in 22-1/2 hours at 45°C (113°F) giving a total solids content of 33.1 percent.

The final resin is then prepared by mixing the following:

Latex (from reaction above)	31.9
Acrylonitrile (or methacrylonitrile)	70
Ethyl acrylate	30
Potassium persulfate	0.06
Emulsifier	3.0
n-dodecyl mercaptan	1.0
Ethylene diamine tetracetic acid	0.5
Water	200

Adjust to pH7 using potassium hydroxide. Twenty hours polymerization time (absence of oxygen) at 60°C (140°F) results in 97 percent conversion to 33 percent solids.

The polymer is then coagulated using aluminum sulfate, washed and dried. At this point the dried polymer chips are then probably densified and passed to an extruder for processing into pellets.

Manufacture - The generalized batch process description for emulsion polymerization shown below is taken from EPA. Development Document No. 440/1-73/010 (16) along with a generalized flowsheet shown as Figure III-16.

A batch process, as shown in Figure III-16, is commonly used. Typical reactor size is 19 cu m (5000 gal.). The batch cycle consists of the continuous introduction of a water-monomer emulsion to the stirred reactor. Polymerization occurs at about the rate of monomer addition; the heat of reaction is removed to cooling tower water circulated through the jacket. The reactor is vented through a condenser for monomer recovery; and the condensate, including any water, is returned directly to the vessel. On completion of the batch, a short "soaking" time is allowed for completion of the reaction, and water is then added to dilute to the desired end composition. The batch is drawn off through a screen to product storage. Oversize screenings (a very small amount) are disposed of to landfill.

Monomers, the principal raw materials, are often protected during shipping and storage by an inhibitor, such as catechol, which may be removed prior to polymerization by washing. This contributes to the waste water load.

Waste Water Generation - Sources of waste water from a typical emulsion polymerization include the following:

- Reactor cooling water
- Cooling tower and boiler blowdown
- Monomer washing
- Liquid or solid waste from monomer stripping or recovery operations
- Discarded Latex batches
- Coagulant wastes
- Startup, spills, etc.
- Demineralizer wastes
- Possible liquid wastes from monomer scrubbing (16, 51, 48).

Other Pollutants

Organic nitrogen occurs as a result of losses from dissolution and emulsification of reactants. Cyanides will be detectable by analytical methods due to the presence of acrylonitrile.

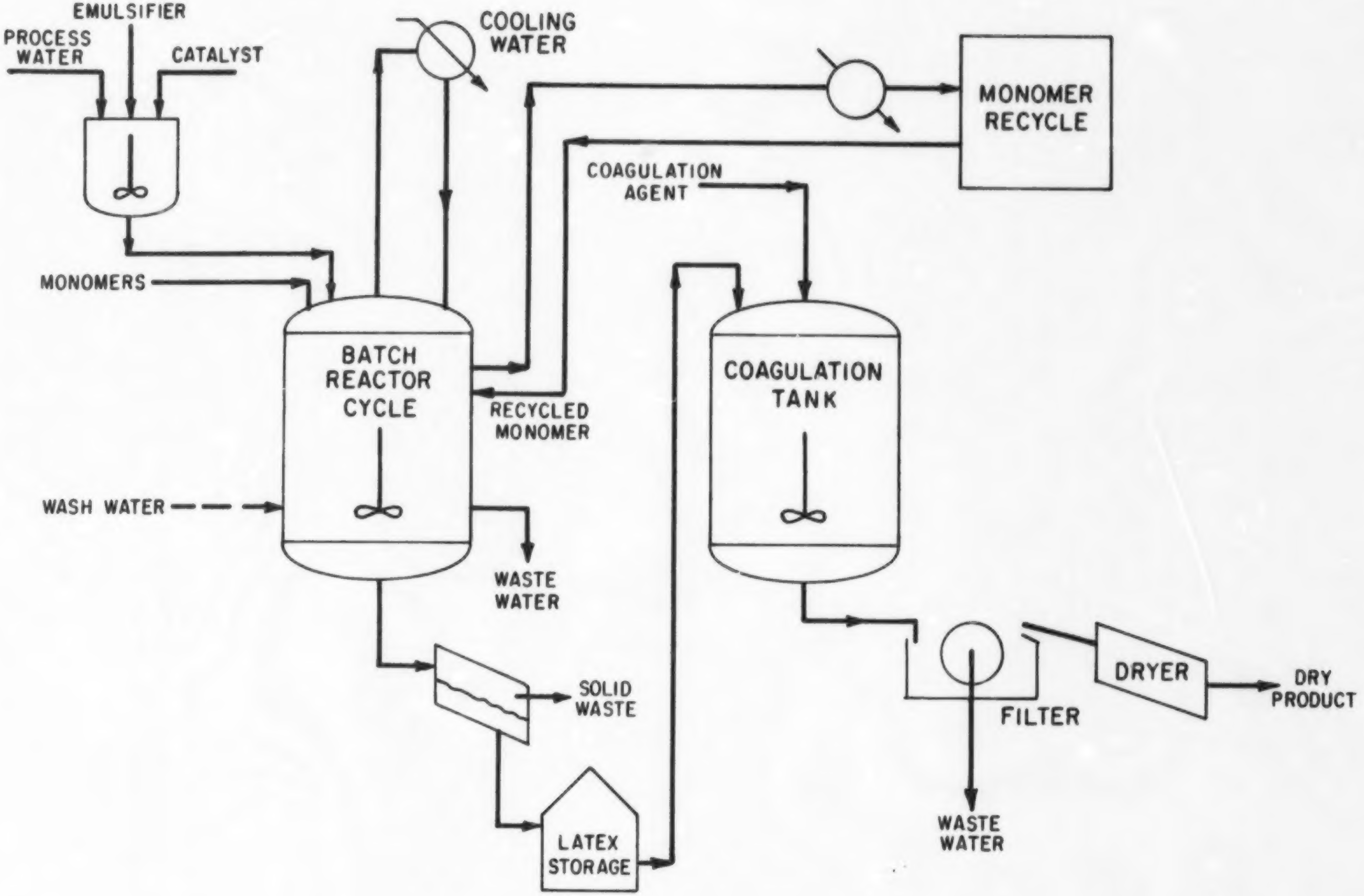

EMULSIFIER
PROCESS WATER
CATALYST
MONOMERS
WASH WATER
COOLING WATER
BATCH REACTOR CYCLE
RECYCLED MONOMER
WASTE WATER
SOLID WASTE
LATEX STORAGE
MONOMER RECYCLE
COAGULATION AGENT
COAGULATION TANK
FILTER
WASTE WATER
DRYER
DRY PRODUCT

FIGURE III-16 [illegible]ER RESIN PRODUCTION – EMULSION POLYMERIZATION PROCESS

Parylene Polymers

Parylene is produced by vapor-phase polymerization and deposition of paraxylylene (or its substituted derivatives). The polymers are highly crystalline, straight-chain compounds with a molecular weight of approximately 500,000. It is extremely resistant to chemical attack, exceptionally low in trace metal contamination, and compatible with all organic solvents used in the cleaning and processing of electronic circuits and systems. Although parylene is insoluble in most materials, it will soften in solvents having boiling points in excess of 150°C (302°F). It is also being used for moisture barrier coatings on discrete components such as resistors, thermistors, thermocouples, fast responding sensing probes, and photocells.

Unlike most plastics, parylene is not produced and sold as a polymer. It is not practical to melt, extrude, mold or calender it as with other thermoplastics. Further, it cannot be applied from solvent systems since it is insoluble in conventional solvents.

Parylene polymers are prepared from di-p-xylylene and dichlorodip-xylylene, through a process called pyrolytic vapor deposition polymerization. Di-p-xylylene and the chloro derivative dichlorodi-p-xylylene are white, high melting crystalline solids. Di-p-xylylene has a melting point of 284°C (543°F) and a density of 1.22 g/cm^3. Dichlorodi-p-xylylene has a melting point of 140-160°C (284-320°F) and a density of 1.3. Both are insoluble in water. The reactions are illustrated in Figure III-17, Equation 1.

Unsubstituted di-p-xylylene can be readily purified by recrystallization from xylene. Dichlorodi-p-xylylene is a mixture of isomers as prepared by chlorination of di-p-xylylene. It is not necessary to separate these isomers since, after pyrolysis, only chloro-p-xylylene results regardless of which isomeric dimer is used as starting material.

The polymerization process is exceptional in that it takes place in two completely distinct and separate steps. The first involves the cleavage of the two-methylene-methylene bonds in di-p-xylylene by pyrolysis to form two molecules of the reactive intermediate, p-xylylene. This latter molecule is stable in the vapor phase but, in the second step, spontaneously polymerizes upon condensation to form high molecular-weight poly(p-xylylene).

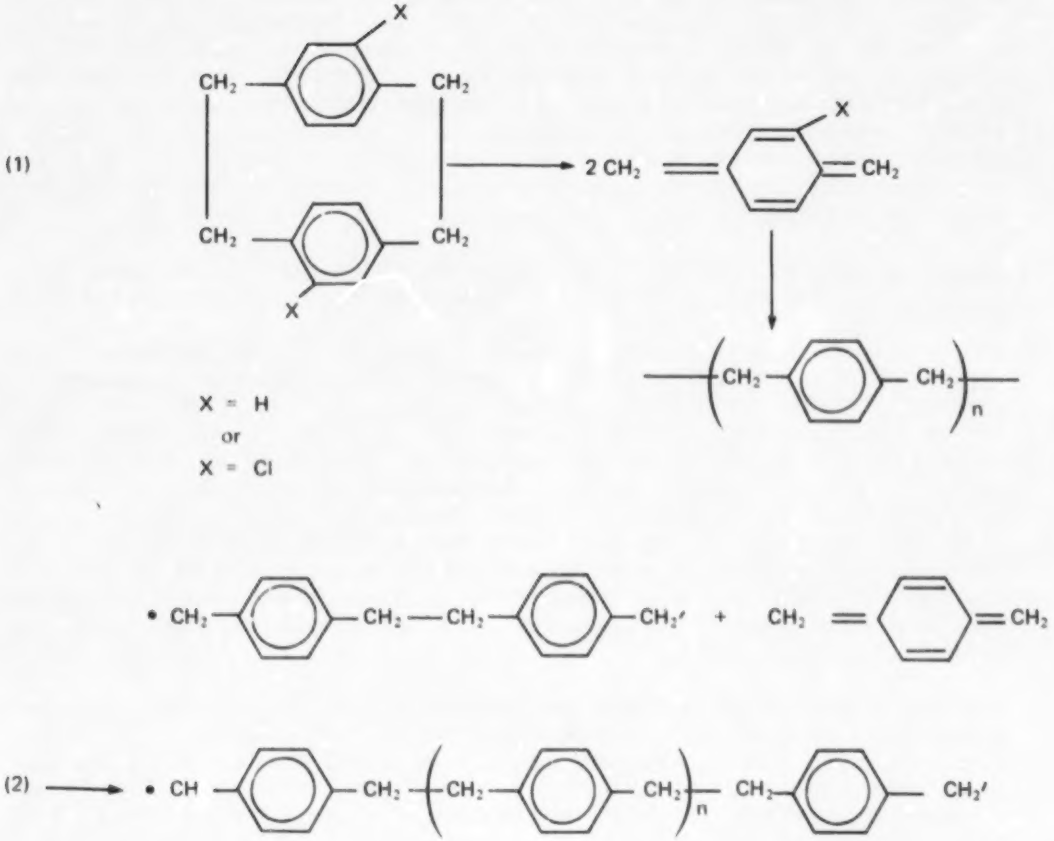

(1)
X
CH₂
CH₂
CH₂
CH₂
X
2 CH₂
X
CH₂
X = H
or
X = Cl
CH₂
CH₂
n
• CH₂
CH₂
CH₂
CH₂'
+
CH₂
CH₂
(2)
• CH
CH₂
CH₂
CH₂
n
CH₂
CH₂'

FIGURE III–17 TYPICAL REACTIONS TO FORM PARYLENE POLYMERS

The polymerization step proceeds by a free-radical mechanism in which, as a first step, two molecules of p-xylylene condense on a surface and react to form a diradical intermediate.

The first step is probably reversible. However, subsequent reaction with p-xylylene by addition to either end of the reactive diradical of the intermediate results in the formation of stable species (Figure III-17, Equation 2) in which n is 1, 2, or 3. Growth then progresses by addition of p-xylylene to each end of the radical. Growth is terminated by reaction of the radical end groups with reactive sites in other growing polymer chains, by reaction of the free-radical sites with chain transfer agents (e.g., oxygen or mercaptans), or by the reactive sites becoming buried in the polymer matrix.

This proposed method of polymerizing p-xylylene suggests that the rate of polymerization should be markedly increased by lowering the temperature of the deposition surface to increase the rate of condensation and, therefore, the concentration of molecules of p-xylylene in the condensed phase. This has also been shown to be the case, and relative polymerization rates of 1, 10, and 100 were observed for p-xylylene on surfaces maintained at 30, 0, and -40°C (86, 32, and -40°F), respectively, and at equivalent monomer concentrations in the vapor phase. These data provide strong evidence that the rate determining step in the polymerization is condensation of a p-xylylene molecule in the vicinity of a growing free radical, and that addition of the condensed molecules to the reactive site is very rapid in comparison.

Manufacture - Manufacture is accomplished in a batch process requiring relatively simple equipment (see Figure III-18). For example, the reactions may be carried out in a 61 cm (24 in.) section of 28 cm (11 in.) I.D. Vycor tubing. The first 15 cm (6 in.) of the tube serves as a distillation zone, and the following 46 cm (18 in.) section as the pyrolysis zone. The pyrolysis tube is connected to a glass deposition chamber. System operating pressure is in the range of 1 Torr. The distillation zone is maintained at temperatures ranging from 140-220°C (284-428°F), depending upon the derivative. The pyrolysis zone is heated to 600°C (1112°F) and the deposition chamber is usually held at room temperature. With some derivatives, it is heated as high as 160°C (320°F) to permit deposition of polymer over a fairly broad area.

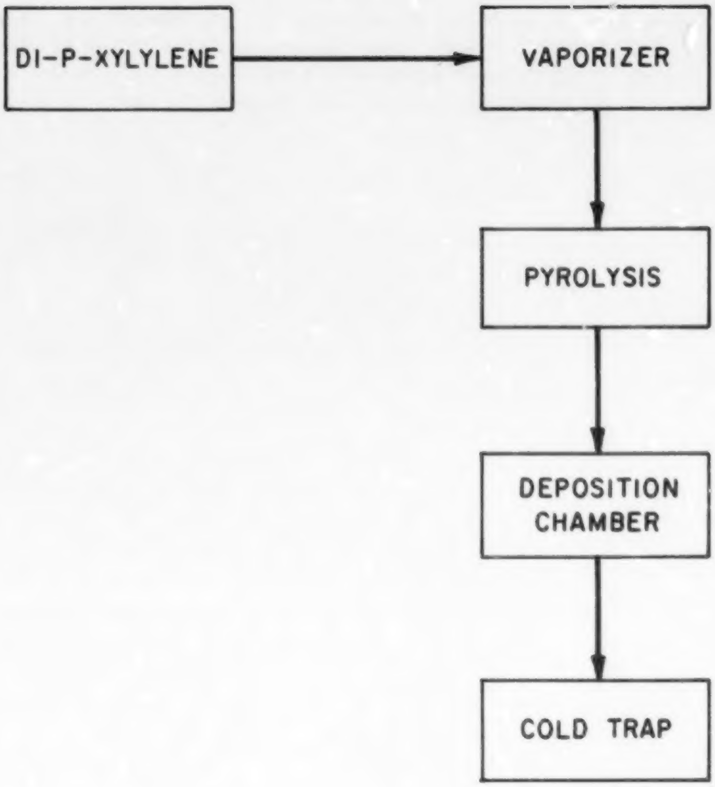

DI-P-XYLYLENE
VAPORIZER
PYROLYSIS
DEPOSITION CHAMBER
COLD TRAP

FIGURE III-18 PARYLENE PRODUCTION

Deposition chambers of virtually any size can be constructed. Those currently in use range from 0.0082-0.459 cu m (500-28,000 cu in.). Large parts up to 1.5 m (5 ft) long and 46 cm (18 in.) high can be processed in this equipment. The versatility of the process also enables the simultaneous coating of many small parts of varying configurations.

Waste Water Generation - The waste water generation from the manufacture of parylene is minimal since it requires no catalysts or solvents. Any waste water generated will be that from the washing and cleaning of processing equipment, which with housekeeping and operational procedures can be contained in the process area. Provided the cold trap is efficient, air pollution would be minimal (27, 34).

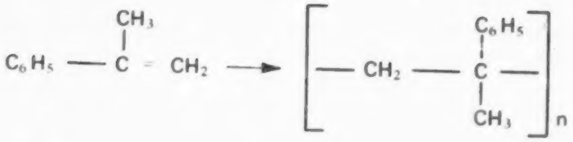
Poly-Alpha-Methyl Styrene

The poly(alpha-methyl styrene) homopolymer is apparently of little commercial importance. The homopolymer has a low ceiling temperature (61°C or 141.8°F), and thus depolymerization can occur easily during fabrication. In addition, the homopolymer is difficult to fabricate because of its high melt viscosity.

Radical polymerization of the pure monomer, alpha-methyl styrene, proceeds very slowly and is not a practical technique for production of this product. Homopolymers are instead prepared by anionic catalysis of the monomer. Polymerizations by free alkali metals are included in this category since a free radical propagation is apparently not involved. The polymerization of alpha-methyl styrene is readily catalyzed by metallic potassium. The polymerization proceeds as shown in Figure III-19.

Recent literature articles report additional polymerization techniques, including: radiation- and photo-induced polymerization of pure alpha-methyl styrene; increased polymerization rate and slightly increased degree of polymerization upon the application of an electric field for pure alpha-methyl styrene; and grafting by irradiation of alpha-methyl styrene to other polymers for the purposes of physical property modification. It is doubtful that these techniques have yet been applied on a commercial scale, however. Those copolymerizations utilizing alpha-methyl styrene which are carried out on commercial scale are accomplished by radical polymerization. In styrene copolymers or terpolymers the presence of alpha-methyl styrene results in a stiffening of the polymer chain. Usually, higher polymer fabrication temperatures are required (and can be tolerated) for these materials.

Manufacture - Adequate information is not available on commercial methods used, if any. Presumably, small batch processing may be employed (25).



$$C_6H_5-\overset{CH_3}{\overset{|}{C}}=CH_2 \longrightarrow \left[-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{C_6H_5}{|}}{C}}-\right]_n$$

FIGURE III–19 TYPICAL REACTION TO FORM ALPHA-METHYL STYRENE

Polyamides

Materials considered to fall in this category include nylons other than Nylon 66 or 6, which were covered in EPA Development Document No. EPA 440/1-73/010 (16). Thus, the category would include Nylon 6/12, Nylon 11, and other polyamides having special structures. Among resins produced in the U.S.A. are Nylon 6/12 (DuPont) and Nylon 11 (Rilsan, Inc.).

Manufacture and Waste Water Generation - Nylon 6/12 is produced in equipment used regularly for production of Nylon 6/6. The product is based on sebacic acid rather than adipic. The process is operated under slightly different conditions than those used for Nylon 6/6. Wastes from the two processes are similar.

Nylon 11 is produced by polymerization of 11-amino undecanoic acid in a process that is comparable to that used for Nylon 6. In the production of Nylon 11, the reaction is such that very little free monomer remains when polymerization is complete. Wastes developed in the process are negligible (41).

Polyaryl Ether (Arylon)

The polyaryl ethers, also known as the polyphenyl ethers or polyphenylene oxides are a new class of polymers. They have the structure shown in Figure III-20, Equation 1, where Ar is an aromatic radical and R may be aromatic or aliphatic. The best known examples of this type of polymer are the thermosetting epoxy resins. Recently, several new polymeric ethers have become commercially important as thermoplastics. These polymers have outstanding hydrolytic resistance, and most of them are unaffected by corrosive environments.

The polyaryl ether resins are made by the oxidative coupling of hindered phenols. The reaction of 2,6-dimethyl phenol to produce polyphenylene oxide is illustrated in Figure III-20, Equation 2. The di-substituted phenol, copper salt, and amine are dissolved, and oxygen is passed through the solution producing the polyphenylene ethers and a minor amount of diphenyl quinone (Figure III-20, Equation 3). The polymer obtained is an extremely high molecular weight material, has a useful temperature of -170°C to +190°C (-274°F to +374°F), and is chemically inert.

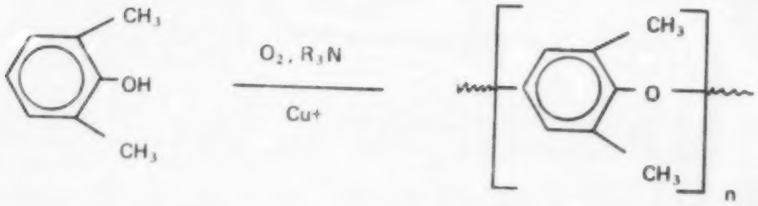
An alternative method of producing the polyphenylene ethers is the oxidation of p-bromophenol. A solution of 2,6-dimethyl-4-bromophenol in aqueous potassium hydroxide is reacted with potassium-ferricyanide, producing poly-2,6-dimethyl-1,4-phenylene ether.

One manufacturer produces poly-2,6-dimethyl-1,4-phenylene ether by another method, the copper-catalyzed oxidation of 2,6-xylenol. The polymer product is marketed under the trademark PPO. The commercial polyphenylene ether is a linear polymer having a molecular weight of 25,000 to 30,000. The electrical properties of PPO (R) are such that the material has been used extensively for high-frequency insulation of electrical equipment. Because PPO (R) can be autoclaved in medical sterilizers, it is used to replace glass and stainless steel in a variety of medical and surgical instruments in hospital utensils. It is also employed in household appliances, in food processing equipment and in plumbing fittings.

A modified form of polyphenylene oxide resins has been introduced under the trademark NORYL, also by General Electric. This material is based on polyphenylene technology and is intended for applications not requiring performance of polyphenylene oxide. The properties of PPO (R) and NORYL (R) are given in Table III-6.

(1) $\left[\mathrm{ArO{-}R{-}O}\right]_n$

(2)


CH₃
OH
CH₃
O₂, R₃N
Cu+
CH₃
O
CH₃
n

(3)

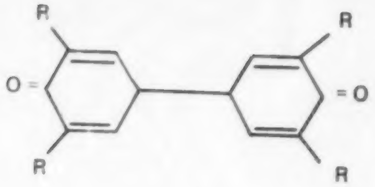


FIGURE III–20 TYPICAL REACTIONS TO FORM POLYARYL ETHER

TABLE III-6

PROPERTIES OF POLYARYL ETHERS

Property	PPO (R)	NORYL (R)
Density	1.06	1.06
Tensile strength, psi kg/sq cm	111,000 740	9,600 675
Elongation, %	80	20
Tensile modulus, psi x 10^5 kg/sq cm x 10	3.8 0.27	3.55 0.25
Impact strength notch, ft-lb/in. Joules/cm	1.5 0.8	1.3 0.7
Heat deflection temp., °F at 264 psi fiber stress	375	265
Heat deflection temp., °C at 18.6 kg/sq cm	190.5	129.5
Dielectric constant, 60 cycles	2.58	2.64

A typical synthesis from the literature is as follows. Oxygen was passed for 10 minutes into a reaction mixture containing 5 g of 2,6-dimethyl phenol, 1 g of Cu_2Cl_2 and 100 ml of pyridine. During the course of the reaction, the temperature rose to a maximum of 70°C (158°F) and no water was removed. The product was precipitated by pouring the reaction mixture into about 500 ml of dilute hydrochloric acid and was separated by filtration. The product, poly-2,6-dimethyl-1,4-phenylene ether, was produced in substantially quantitative yields.

This product had a molecular weight in the range of 300,000 to 700,000 and did not melt at 300°C (572°F). The powder produced on precipitation could be molded, calendered, or extruded under pressure.

Manufacture - Manufacturing processes for polyaryl ethers have not been discussed in the literature. By analogy to the bench-scale syntheses, solution polymerization in water is probably practiced for polyphenylene oxides.

Waste Water Generation - Waste water effluents will contain small fractions of all components of the reaction mixture, including monomers, catalysts (copper-salts), and amine and possibly the by-product diphenyl quinone, or other reactants and catalysts depending upon the process of interest. In general, there is one mole of water of reaction produced per mole of oxide linkage or, for poly-2,6-dimethyl-1,4-phenylene ether, 159 mass units of water per 1000 mass units of polymer product (23).

Polybenzimidazoles

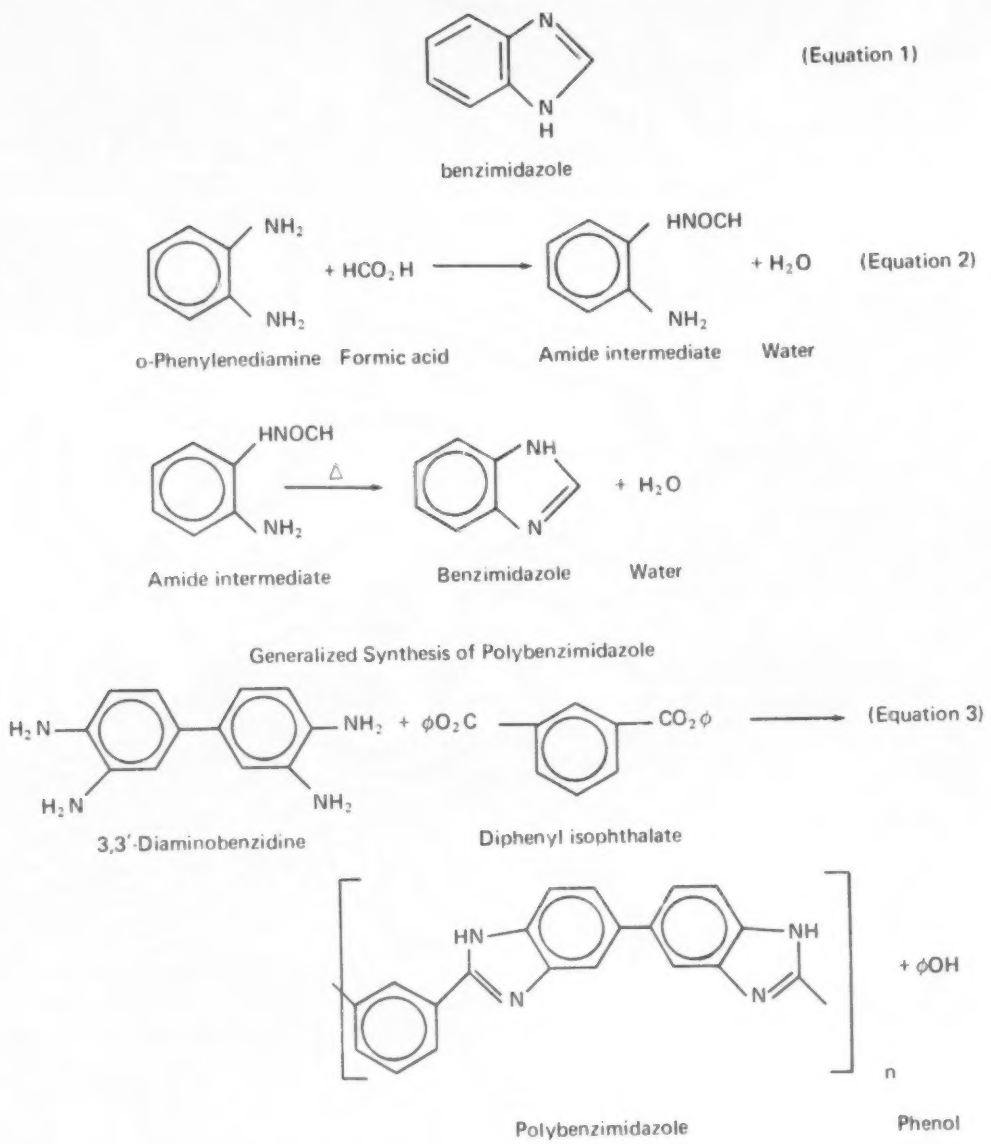
The polybenzimidazoles are polymers incorporating the benzimidazole ring into the polymer backbone as shown in Equation 1 of Figure III-21. These polymers are notable for their stability to oxidative attack at high temperatures. They have high molecular weights and excellent resistance to hydrolytic attack in acidic or basic media.

Essentially, the benzimidazole is formed by the reaction of a 1,2-aromatic diamine with a carboxyl group. The reaction may be written as shown in Equation 2 of Figure III-21.

The first polybenzimidazoles, described in a patent in 1959, were synthesized by condensation of aromatic bis-o-diamines with aliphatic dicarboxylic acids in a manner analogous to the preparation of benzimidazoles. This polymer, which incorporated an aliphatic linkage, gave the first indication that high temperature resistance might be achievable in these polymers. This synthesis was followed by that of completely aromatic polybenzimidazoles in the belief, later justified, that thermal and oxidative properties would be improved in a totally aromatic system.

The initial work with the aromatic polybenzimidazoles involved reaction of an aromatic tetraamine with a diphenyl ester of an aromatic dicarboxylic acid -- in particular, the reaction of 3,3'-diaminobenzidine and the phenyl ester of isophthalic acid. The reaction is illustrated in Equation 3 of Figure III-21. Subsequent work extended to the synthesis of a number of polymers from other acid derivatives. From this initial exploratory work, 3,3'-diaminobenzidine and isophthalic or blends of isophthalic and terephthalic derivatives were selected as most promising. These acids are illustrated in Table III-7.

Polybenzimidazoles have been synthesized to high molecular weight by solution, melt, or solid state polymerization. Solution condensation can take place in either an organic solvent having a boiling point sufficiently high for the reaction to proceed, or in polyphosphoric acid. A typical high-boiling organic solvent is either phenol or m-cresol. Phenol has the ability to provide an easier, more complete polymerization than most solvents. It is necessary to conduct all condensations under inert atmosphere to prevent oxidation of the tetraamine. Condensations have been reported in which solvents such as dimethylacetamide,


N
N
H
benzimidazole
(Equation 1)
NH₂
NH₂
+ HCO₂H
HNOCH
NH₂
+ H₂O
(Equation 2)
o-Phenylenediamine
Formic acid
Amide intermediate
Water
HNOCH
NH₂
Δ
NH
N
+ H₂O
Amide intermediate
Benzimidazole
Water
H₂N
H₂N
NH₂
NH₂
+ φO₂C
CO₂φ
(Equation 3)
3,3′-Diaminobenzidine
Diphenyl isophthalate
HN
N
NH
N
n
+ φOH
Polybenzimidazole
Phenol

Generalized Synthesis of Polybenzimidazole

FIGURE III–21 TYPICAL REACTIONS TO FORM POLYBENZIMIDAZOLES

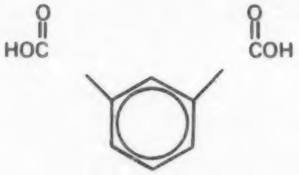
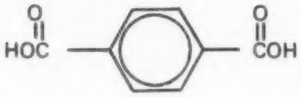
Isophthalic Acid	
Terephthalic Acid	

TABLE III–7 ACIDS WHOSE DERIVATIVES ARE USED IN POLYBENZIMIDAZOLE SYNTHESIS

dimethylformamide, dimethylsulfoxide, N-methylpyrrolidone, phenol, and cresol were used. Polyphosphoric acid has been investigated because the oxidation sensitivity of the tetraamines could be circumvented by use of the tetrahydrochloride salt. Upon heating in an inert atmosphere, hydrogen chloride is evolved at about 140-150°C (284-302°F), giving a solution of tetraamine and polyphosphoric acid.

Melt condensation for preparation of polybenzimidazoles has been investigated in some detail. Upon application of heat, the mixture of monomers melts, and shortly thereafter the evolution of phenol becomes noticeable and rapid. Continued heating results in increasing viscosity until the reaction mixture solidifies. At this point vacuum is applied to remove as much evolved phenol as possible. After the polymer has been cooled to room temperature, it is pulverized, replaced in the polymerization tube, and the polymerization is completed by slowly heating to 350-400°C (662-752°F) in vacuo. Thus, the critical phase of the polymerization, in which high molecular weight is achieved, takes place as a solid state reaction.

Many polybenzimidazoles have been synthesized since the original disclosures. The greatest impetus was provided by the work involving the fully aromatic systems.

In general, if equimolar quantities of reactants are employed, the polymerization will continue with heating to produce high molecular weight polymers soluble only in formic or sulfuric acids. These cannot conveniently be processed further. Accordingly, the reaction may be interrupted at some intermediate stage to produce soluble, low-melting compounds which can be applied in the liquid phase. Alternatively, through the use of an excess of amine, an amine-terminated prepolymer may be produced, which is then combined with an acid-terminated prepolymer, with the remainder of the polymerization being subsequently conducted either from solution or as a hot melt. During the final polymerization, there will be the evolution of considerable volumes of volatiles, which must be removed from the polymerizing structure. Thus, at high pressures, low molecular weight polymers may be developed as a result of entrapped volatiles. For some purposes, high volatile content is desirable. For example, porous laminates provide better strength properties than do the more dense structures. For other purposes, systems with low volatile contents have been developed. The envisioned applications for polybenzimidazoles are as high temperature adhesives and laminating resins for the aerospace industry. They may be employed as secondary structural members in supersonic aircraft, and as adhesives for honeycomb bonding and similar applications. Among the civilian potential of these materials are their use as ultrafiltration and hyperfiltration membranes.

Manufacture - Specific process information on this subject has not been reported in the literature. However, processes are probably scale-ups of the original laboratory synthesis, i.e., solution polymerization in high-boiling organic solvents or in polyphosphoric acid. Melt condensation is practiced for several of the products, wherein processing may proceed only to the low molecular weight, low-melting, soluble compounds which are used in the liquid state. Alternatively, prepolymers may be produced for later polymerization in solution or in bulk.

Waste Water Generation - Process wastes will include the water and the phenol evolved in polybenzimidazole synthesis: 2 moles of each per mole of benzimidazole group. For the condensation with the isophthalic or terephthalic ester, this corresponds to 120 mass units water and 610 mass units of phenol per 1,000 mass units of polymer product. In the solution polymerization process in polyphosphoric acid, hydrogen chloride is evolved during the condensation.

The quality of water effluent will depend upon pretreatment, but some dissolved phenol and/or HCl and some monomer reactant will likely be present (29).

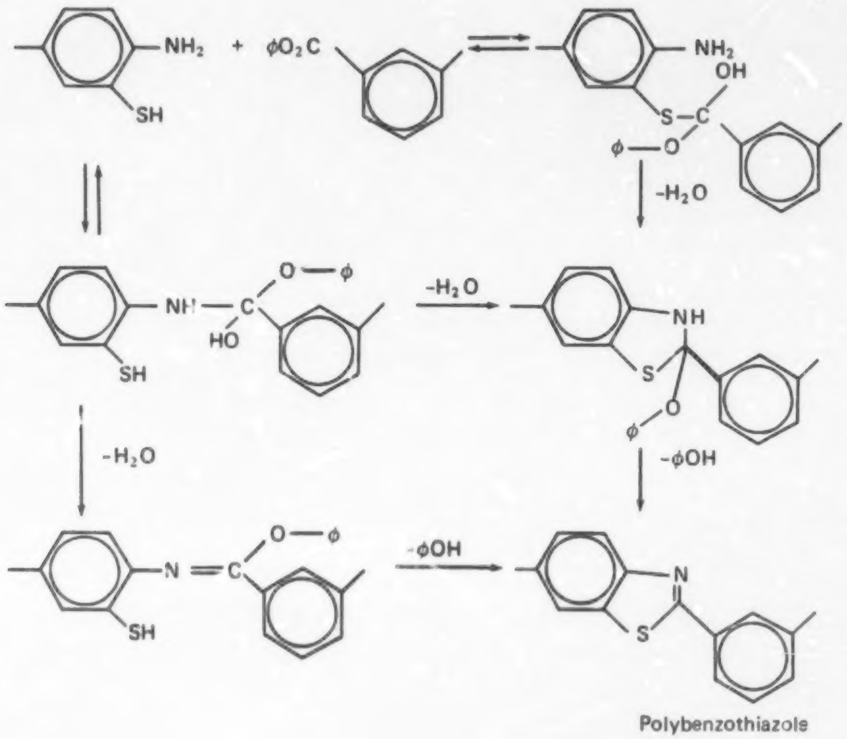
Polybenzothiazoles

Similar to the polybenzimidazoles are the polybenzothiazoles. These polymers are prepared from 3,3'-dimercaptobenzidine and a diacid, a diphenyl ester, a diacid chloride, etc. The reaction sequence is as shown in Equation 1 of Figure III-22 for use in diphenyl esters. Typical of the structures synthesized by this procedure are those shown in Figure III-23. The hydrochloric acid salt of 3,3'-dimercaptobenzidine may also be used along with the diacid chloride, overcoming the problem of sensitivity to air oxidation of the parent mercaptoamine. This is illustrated in Equation 2 of Figure III-22. Many other syntheses of various polybenzothiazoles have also been attempted, some with success. Many of the problems associated with the synthesis of the polybenzimidazoles are common to the synthesis of the polybenzothiazoles and thus synthesis approaches are frequently similar.

Typical reaction conditions for the polymerization to polybenzothiazoles are temperatures of 160-250°C (320-482°F) and times of one to 25 hours.

Waste Water Generation - As with the polybenzimidazoles, the polymerization leads to the release of 2 moles of water per mole of benzothiazole group and 2 moles of phenol if the diphenyl ester is used. For the condensation of the isophthalic ester, this corresponds to 110 mass units water and 550 mass units phenol per 1000 mass units of polymer product (29).

(1)


NH₂
ϕO₂C
SH
NH₂
OH
S—C
ϕ—O
-H₂O
O—ϕ
NH—C
HO
SH
-H₂O
NH
S
O
ϕ
-H₂O
-ϕOH
O—ϕ
N=C
SH
-ϕOH
N
S
Polybenzothiazole

(2)

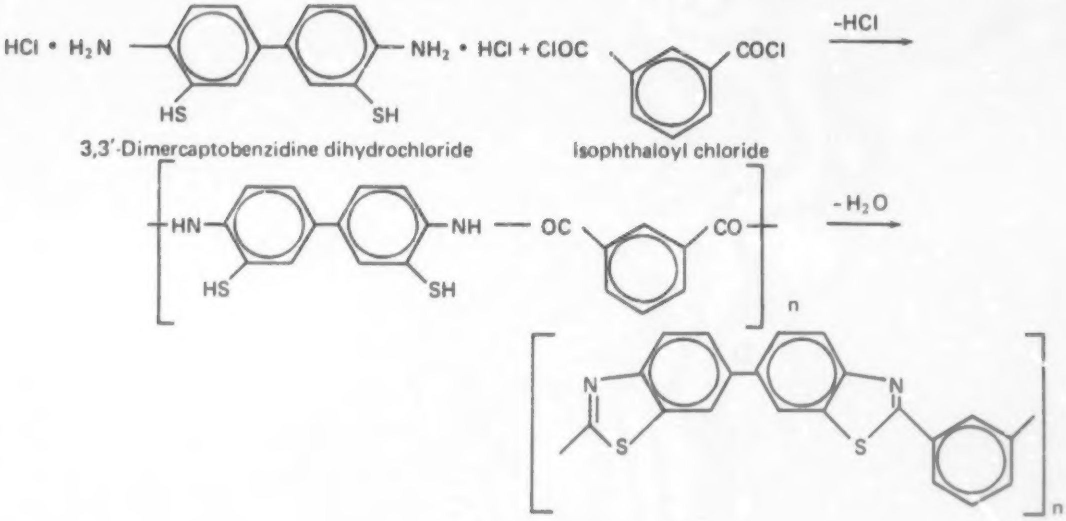
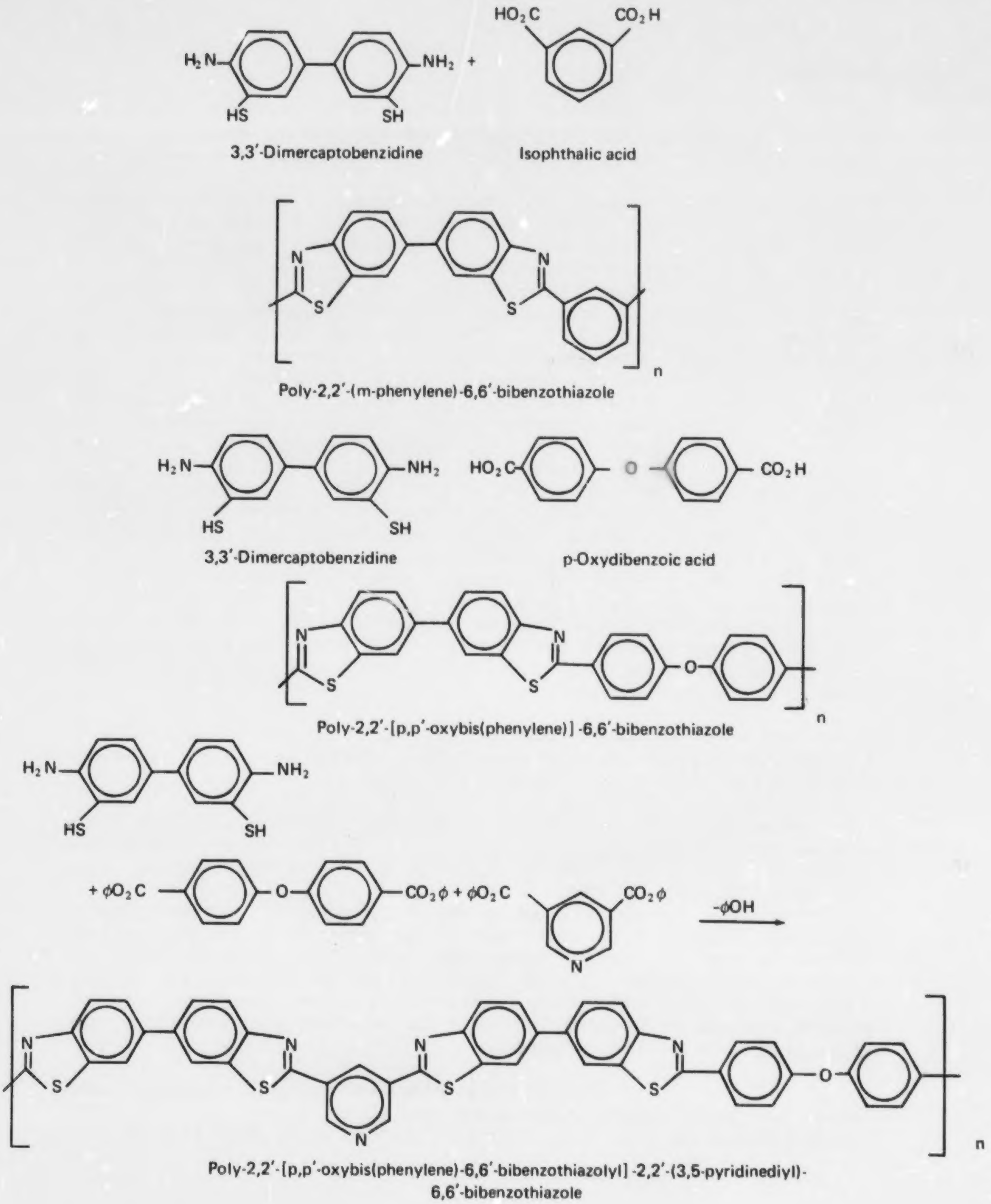

HCl • H₂N
NH₂ • HCl + ClOC
COCl
-HCl
HS
SH
3,3′-Dimercaptobenzidine dihydrochloride
Isophthaloyl chloride
HN
NH — OC
CO
HS
SH
n
-H₂O
N
S
N
S
n

FIGURE III–22 TYPICAL REACTIONS TO FORM POLYBENZOTHIAZOLES



3,3'-Dimercaptobenzidine

Isophthalic acid

Poly-2,2'-(m-phenylene)-6,6'-bibenzothiazole

3,3'-Dimercaptobenzidine

p-Oxydibenzoic acid

Poly-2,2'-[p,p'-oxybis(phenylene)]-6,6'-bibenzothiazole

Poly-2,2'-[p,p'-oxybis(phenylene)-6,6'-bibenzothiazolyl]-2,2'-(3,5-pyridinediyl)-6,6'-bibenzothiazole

H_2N
NH_2
HS
SH
+
HO_2C
CO_2H
N
S
n
O
$+ \phi O_2C$
$CO_2\phi$
$+ \phi O_2C$
$CO_2\phi$
$-\phi OH$

FIGURE III–23 TYPICAL STRUCTURES PRODUCED IN THE SYNTHESIS OF POLYBENZOTHIAZOLES

Polybutene

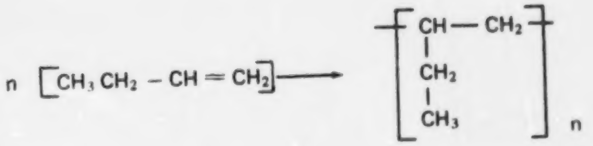
Polybutene can be produced by the polymerization of 1-butene in the presence of catalysts as shown in Equation 1 of Figure III-24. Usually Ziegler-type catalysts are employed.

Manufacture - Polybutene or polybutylene is currently being produced by either of two processes. In the United States, Mobil Chemical Company uses a polymerization process which starts when fresh feed and recycle monomer are combined and passed through a distillation and drying step to remove volatile impurities and water prior to polymerization. The reaction is carried out in the presence of Ziegler-Natta catalysts, and the product stream from the reactor is contacted with water to remove catalyst residues. Water is then separated, the polymer phase is heated and flashed to remove 1-butene for recycle, and the molten polymer is cooled and extruded into pellets. Another process for polymerization of polybutene is utilized by Chemische Werke Huels AG and is also based on the use of Ziegler-type catalysts. In this process, a C-4 feed stream along with recycled butenes from the process is fed to the monomer purification section where butadiene is removed. The resultant 50 percent 1-butene stream (with only trace quantities of butadiene and isobutylene) is then passed to the first of two distillation towers where the high boiling components are removed as bottoms. In the second column low boilers are removed at the top, and the reactants are recovered at the bottom.

The monomer stream next goes to two stainless steel continuous polymerization reactors. Catalyst and solvent are added in the first reactor.

The polymer/solvent slurry from the second step is then washed with water to remove catalyst. The wash water is directed to the waste treatment facility, while the remaining slurry is sent to a centrifuge as a first step in removing the atactic isomer which is produced in the Huels process. Liquid from the centrifuge goes to a distillation column where a waxy substance, atactic polybutylene, is removed as bottoms. (This atactic polybutylene is often used as a carpetbacking material.) The overhead liquid butene stream is cooled and sent to monomer purification and then recycled to the process.

Solid polymer is recovered from the centrifuge, dried, and sent to bins where additives are added prior to extrusion and pelletizing. A flow chart is shown in Figure III-25.



$$n\left[CH_3CH_2-CH=CH_2\right]\longrightarrow\left[\begin{array}{l}-CH-CH_2-\\ \;\;|\\ \;\;CH_2\\ \;\;|\\ \;\;CH_3\end{array}\right]_n$$

FIGURE III–24 TYPICAL REACTION TO FORM POLYBUTENE

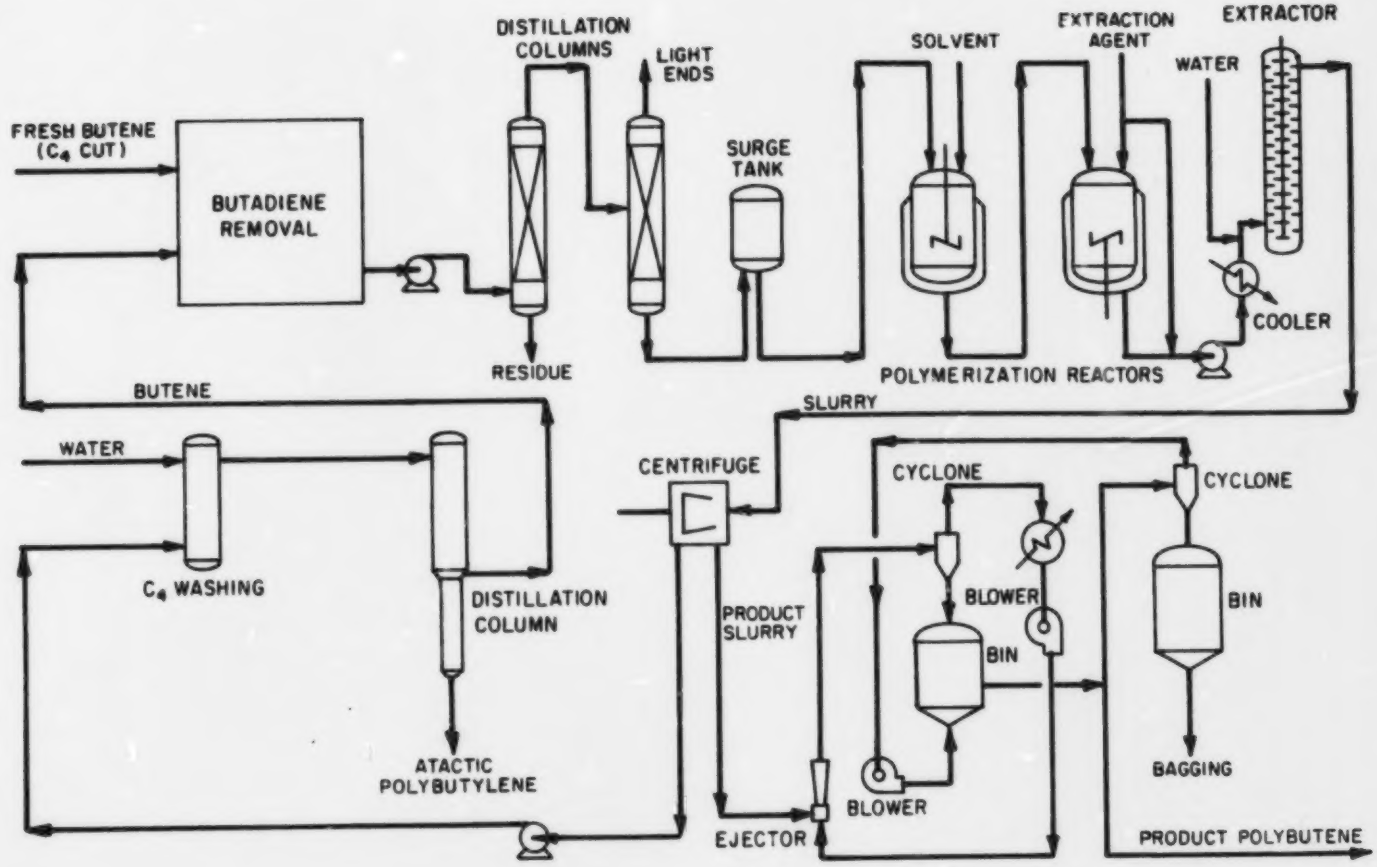

FRESH BUTENE (C_4 CUT)
BUTADIENE REMOVAL
DISTILLATION COLUMNS
LIGHT ENDS
RESIDUE
SURGE TANK
SOLVENT
EXTRACTION AGENT
WATER
EXTRACTOR
COOLER
POLYMERIZATION REACTORS
BUTENE
SLURRY
WATER
C_4 WASHING
DISTILLATION COLUMN
ATACTIC POLYBUTYLENE
CENTRIFUGE
PRODUCT SLURRY
EJECTOR
CYCLONE
BLOWER
BIN
BLOWER
CYCLONE
BIN
BAGGING
PRODUCT POLYBUTENE

FIGURE III-25 POLYBUTENE PRODUCTION – HUELS PROCESS

There are several important differences between the Mobil and Huels processes. The Mobil process, which is based on a relatively pure 1-butene monomer stream, is carried out in the presence of excess butene monomer. This enables the reaction to be carried out without the need for solvent. The Huels process is based on a raw C-4 cut, which requires purification prior to polymerization. The Mobil process does not produce atactic isomer, a portion of the polybutene produced by the Huels process is atactic.

Waste Water Generation - The major aqueous wastes are likely to be minimal in both processes, and especially so in Mobil's process. In the Huels process, liquid residues from columns and some aqueous wastes from C-4 washing are likely (25).

Polycarbonates

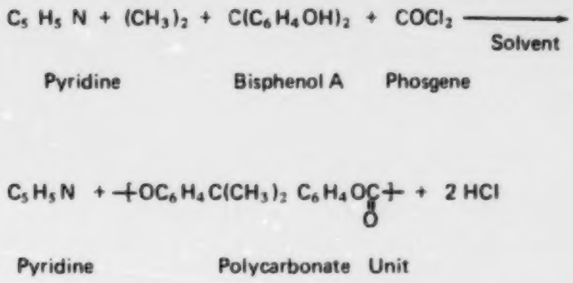
Polycarbonates are a special variety of linear thermoplastic polyesters in which a derivative of carbonic acid is substituted for the acid and a diphenol is substituted for the glycol. Polycarbonates are end products in themselves, undergoing thermoplastic processing utilizing the conventional equipment of the plastic industry. By far the most important polycarbonates from the commercial point of view are aromatic polycarbonates derived exclusively from the reaction of bisphenol A with phosgene. In addition, aliphatic or aliphatic-aromatic polycarbonates may be derived, but indications are that they find little industrial usage. Thus they will not be discussed.

Phosgene is a liquefied gas, boiling at 7.6°C (45.7°F), and is only very slightly soluble in water. Bisphenol A is a solid melting at 152°C (305°F) and is soluble in water to the extent of 3000 mg/liter at 85°C (185°F). The polymerization may be carried by means of the following mechanisms: condensation, interfacial, and transesterification. Of the three, condensation is preferred. Interfacial polymerization is seldom used for it is inconvenient and slow, and in order to achieve sufficiently high rates of transesterification, the reaction conditions must be so drastic that a portion of the polycarbonate is decomposed.

The reaction between the two raw materials takes place under alkaline conditions in the presence of catalyst and pyridine as shown by Equations 1 and 2 in Figure III-26.

In contrast to base-free condensation, which proceeds only at high temperatures in the presence of special catalysts and yields polymers with insufficient molecular weights, condensation in the presence of basic substances proceeds at high rates at room temperature to give high molecular weight polycarbonates. As shown in the above equation, two moles of hydrochloric acid are formed per mole of phosgene consumed. To maintain basic conditions in the reactant mix, the hydrochloric must be either neutralized or consumed. Pyridine is added, usually in excess, to act as an acid acceptor and so that the resulting polycarbonate forms a more or less viscous solution. Alternatively, a good portion of the pyridine may be replaced by an organic solvent in which the polycarbonate is soluble. The reactant is strongly catalyzed by Lewis acids such as aluminum chloride, aluminum isopropoxide, stannic chloride and titanium tetrachloride. Suitable reaction media solvents are the chlorinated aromatic hydrocarbons, such as

(1)


Pyridine
Bisphenol A
Phosgene
Solvent
Pyridine
Polycarbonate Unit

$$C_5H_5N + (CH_3)_2 + C(C_6H_4OH)_2 + COCl_2 \xrightarrow[\text{Solvent}]{}$$

$$C_5H_5N + \left[OC_6H_4C(CH_3)_2C_6H_4O\underset{\underset{O}{\|}}{C} \right] + 2\,HCl$$

(2) $[C_5H_5N] + HCl \longrightarrow C_5H_6NCl$

FIGURE III–26 TYPICAL REACTION TO FORM POLYCARBONATE

chlorobenzene, methylene chloride, or o-dichlorobenzene. A typical catalyst is benzyl triethyl ammonium chloride. It is important to use equimolar quantities of phosgene and bisphenol A, since the molecular weight of the product will depend on the ratio of the starting materials. It is also important to avoid the presence of substances such as monofunctional alcohols or phenols which act as chain terminators. The molecular weight is also indirectly dependent on possible concurrent side reactions, which in turn depend on the usual parameters such as temperature, time, and reactants. In choosing the solvent, chlorobenzene is preferable since the pyridine hydrochloride formed is insoluble in this medium and may be readily separated by filtration. Traces of the hydrochloride that are in solution may be removed by distillation.

Manufacture - The process scheme is shown in Figure III-27. The bisphenol A is charged with excess pyridine and a solvent such as methylene chloride into the vessel. Phosgene is vaporized in a still, and then bubbled through the reaction mixture. Total moles of phosgene fed are in slight excess of the moles of bisphenol A charged. Phosgene and bisphenol react to form the carbonate monomer, which in turn polymerizes. Reacting mixture is kept under 40°C (104°F); residence time in the vessel is 1 to 3 hours. The reaction can be controlled through any of several variables, including residence time, temperature, and proportions of the components introduced. Component purity also has great effect on the reaction.

Reacted mixture, consisting of the polymer, pyridine hydrochloride, and unreacted pyridine in solvent, is fed to water wash tanks. Wash water and hydrochloric acid are added here, the acid reacting with residual pyridine. Additional solvent may also be introduced at this stage to lower the viscosity of the mixture.

The next step is the removal of water and pyridine hydrochloride by decantation or the equivalent. The aqueous phase goes to pyridine recovery; the solvent phase, containing the dissolved polymer, goes to an agitated precipitation tank.

Here the polymer is precipitated by addition of an organic "antisolvent" such as an aliphatic hydrocarbon. This forms a solution with the carrier solvent and causes the polymer to precipitate. The resulting slurry goes to a rotary filter, and the separated polymer goes to a hot air dryer where the remaining solvent is removed. The polymer leaves the dryer as a powder and is sent to blending, extrusion,

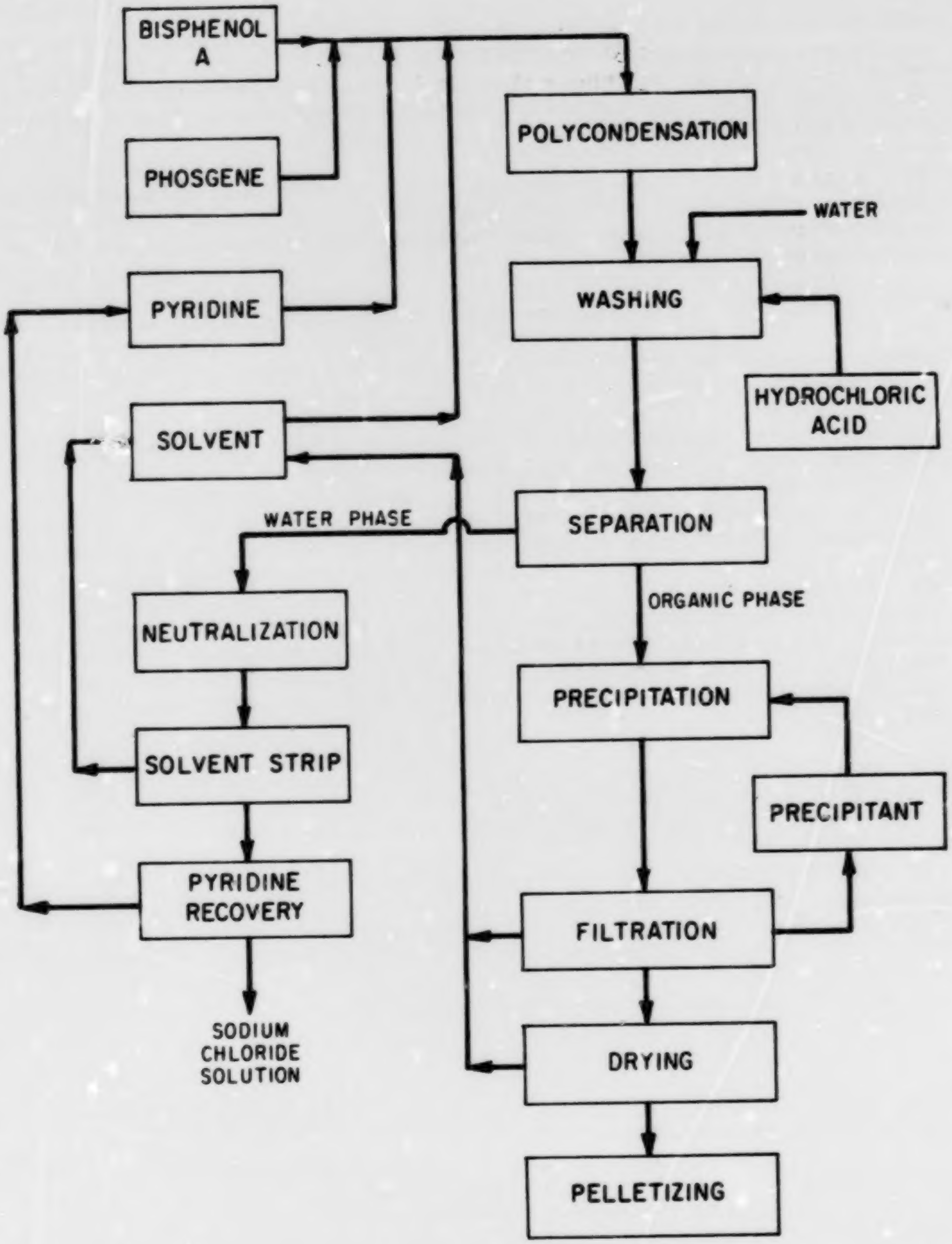

BISPHENOL A
PHOSGENE
PYRIDINE
SOLVENT
POLYCONDENSATION
WATER
WASHING
HYDROCHLORIC ACID
WATER PHASE
SEPARATION
ORGANIC PHASE
NEUTRALIZATION
SOLVENT STRIP
PRECIPITATION
PRECIPITANT
PYRIDINE RECOVERY
FILTRATION
SODIUM CHLORIDE SOLUTION
DRYING
PELLETIZING

FIGURE III-27 POLYCARBONATE PRODUCTION – SEMI-CONTINUOUS PROCESS

and pelletizing. Aqueous pyridine hydrochloride solution is combined with caustic solution in a mix tank for removal of chloride ions as sodium chloride. The stream then goes from the mix tank to a fractionating column where steam strips out any solvent present.

The stripped solution goes to an azeotropic distillation column, and the sodium chloride solution is removed as bottoms and discarded. The overhead stream is an azeotrope consisting of about 43 percent water, 57 percent pyridine.

The azeotrope is condensed and then combined with a breaking agent. The mixture goes to a pyridine distillation column where water-free pyridine is removed overhead. The bottoms are treated to recover the breaking agent.

Waste Water Generation - The waste water originating from the process is principally due to polymer washing. The major substance present in the waste water stream will be sodium chloride. The amount and concentration of sodium chloride will depend upon the excess of pyridine required and the dilution necessary to effect adequate washing. It is expected that the waste waters will be alkaline from excess sodium hydroxide used in the recovery of pyridine. Also, the waste water stream would be expected to contain traces of pyridine, solvents, breaking agents, bisphenol, polycarbonate, and side reaction products (25, 28, 36, 40, 46).

Polyester Resins (Thermoplastic)

The most common polyester is derived from the linear polymer, poly(ethylene terephthalate). The other homopolymer to achieve this polymer, the dihydric alcohol is butanediol rather than ethylene glycol.

The term thermoplastic polyester resin as used in this report refers to the saturated polyester polymers based on poly (ethylene terephthalate) or poly(butylene terephthalate). These polymers are quite different in method of manufacture, chemistry, and areas of application from the unsaturated polyester resins in which a site of unsaturation is incorporated into the polymer chain for subsequent reaction to form a crosslinked structure.

The saturated polyester resins comprise a rapidly growing market of molding materials. These resins are produced by the same polymerization process used to polymerize resin for fiber production. Resin chips are often taken as a side stream from integrated polyester fiber plants. There are, however, some U.S. polyester resin facilities which produce resin alone and are not integrated to fiber production. In addition, there are polyester film facilities which are integrated back to resin production.

The dihydric alcohol most frequently used in the polyester condensation reaction is ethylene glycol. Specific requirements for the dihydric alcohol are that it be quite pure and particularly free from color-forming impurities and traces of strong acids and bases.

The other component can be either dimethyl terephthalate (DMT) or terephthalic acid (TPA). The use of DMT as a polyester raw material is more common. There is a difference in waste products generated during polymerization depending on whether DMT or TPA is used. The use of DMT results in the generation of methyl alcohol either as a waste or by-product stream, whereas the TPA-based polymerization process does not. In either case a waste stream containing unreacted glycol is generated.

The exact nature of the catalysts used in the polymerization process varies somewhat and is regarded as proprietary information. They are, however, known to include acetates of cobalt, manganese, and cadmium.

Manufacture - Many plants still use the batch polymerization process. A typical continuous polymerization process based on DMT consists of a DMT melter, ester exchange vessel, and a polymerization reactor(s). This process is shown schematically in Figure III-28. The alternative system based on TPA involves a direct esterification rather than ester interchange.

In the case of plants producing both resin and fiber, the molten polymer stream from the final reactor is divided. Polymer destined to become resin is chilled by once-through cooling water during a band casting operation and broken up into chip form for shipping. The figure shows polyester resin production from ethylene glycol or butanediol.

Waste Water Generation - Liquid wastes result from the condensation of steam ejector vapors (suction and discharge sides). Process materials present in these streams are methanol and ethylene glycol when ethylene glycol is the diol feed, and methanol and tetrahydrofuran in the case of butanediol feed. In the latter case, when unreacted (excess) butanediol is removed from the process under vacuum, it spontaneously dehydrates to produce tetrahydrofuran (25).

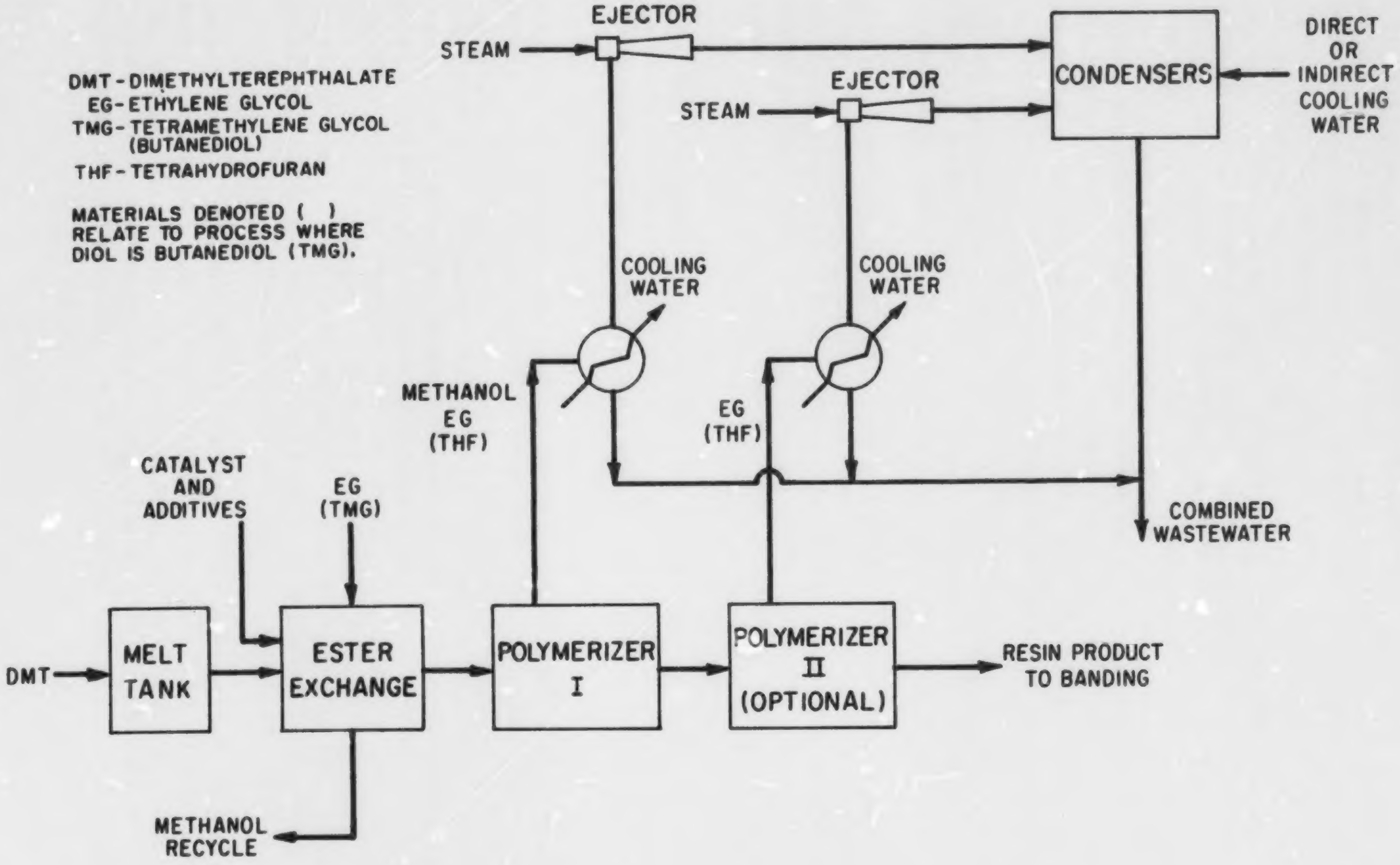

DMT-DIMETHYLTEREPHTHALATE
EG-ETHYLENE GLYCOL
TMG-TETRAMETHYLENE GLYCOL (BUTANEDIOL)
THF-TETRAHYDROFURAN
MATERIALS DENOTED ( ) RELATE TO PROCESS WHERE DIOL IS BUTANEDIOL (TMG).
STEAM
EJECTOR
STEAM
EJECTOR
CONDENSERS
DIRECT OR INDIRECT COOLING WATER
COOLING WATER
COOLING WATER
METHANOL EG (THF)
EG (THF)
COMBINED WASTEWATER
CATALYST AND ADDITIVES
EG (TMG)
DMT
MELT TANK
ESTER EXCHANGE
POLYMERIZER I
POLYMERIZER II (OPTIONAL)
RESIN PRODUCT TO BANDING
METHANOL RECYCLE

FIGURE III-28 THERMOPLASTIC POLYESTER RESIN PRODUCTION

Polyester Resins (Unsaturated)

Unsaturated polyester resins are made by an esterification reaction involving a glycol and both an aromatic dibasic acid and an unsaturated dibasic acid. The unsaturated dibasic acid is used to incorporate an ethylenic linkage into the polymer and is a compound such as maleic acid or fumaric acid. The aromatic dibasic acid can be phthalic acid, isophthalic acid or the like. The glycol is commonly propylene glycol. The basic polyester resin is made typically by a batchwise reaction process in stirred, glass-lined, or stainless steel vessels and is later dissolved in a reactive monomer such as styrene which can crosslink with the ethylenic bonds in the main polymer. The resultant viscous liquid, diluted with styrene, is the current item of commerce known as polyester resin.

The chemical structure of the various materials involved in polyester resin fabrication are shown in Figure III-29, along with a representation of the basic reactions involved.

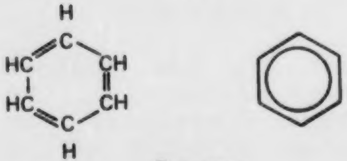
All of the starting materials for polyester resin manufacture are derived from petroleum fractions. The aromatic acids are made from xylenes, and the unsaturated acids are made from benzene by oxidation. The most common glycol, propylene glycol, is made from propylene via oxidation. Styrene is made from benzene and ethylene.

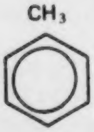
Phthalic acid and maleic acid are both easily dehydrated and are therefore used in the form of anhydrides rather than as acids in order to avoid the costs associated with shipping water.

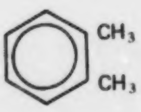
The major use for unsaturated polyester resins is in the manufacture of reinforced plastics. They constitute about 80 percent of all the materials used for reinforced plastic applications. Glass fiber is the most common reinforcing agent, although other reinforcements such as metallic fibers and natural fibers are occasionally used. Typically, glass fiber averages about 35 percent of the weight of the reinforced polyester. Nonreinforced applications for unsaturated polyester resin include molded plastic and resins used for castings, surface coatings, and putty-like compounds used as body solder on automobiles.

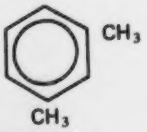
Manufacture - There are two somewhat different procedures for carrying out the polyester polymerization reaction. The differences are related to the manner in which the water of reaction is removed. The fusion process removes the water by passing an inert gas, usually nitrogen, through the

HYDROCARBON STARTING MATERIALS

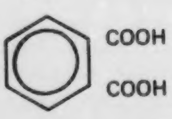

Benzene

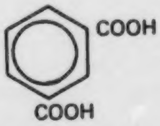

Toluene

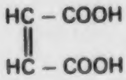

Ortho-xylene

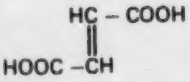

Meta-xylene

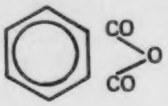
ACIDS

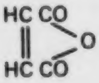

Ortho-phthalic Acid


Iso Phthalic Acid (IPA)


$$\begin{array}{l} HC - COOH \\ \| \\ HC - COOH \end{array}$$
Maleic Acid


$$\begin{array}{r} HC - COOH \\ \| \\ HOOC - CH \end{array}$$
Fumaric Acid (FA)


Phthalic Anhydride (PA)


Maleic Anhydride (MA)

GLYCOLS

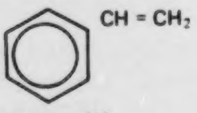
$HO\ CH\ (CH_3)\ CH_2\ OH$

Propylene Glycol (PG)

$HO\ CH_2\ C\ (CH_3)_2\ CH_2\ OH$

Neopentyl Glycol (NPG)

REACTIVE SOLVENT


Styrene (S)

POLYESTERS

$HOOC - R\text{-}COOH + HO - R' - OH \longrightarrow (- OOC - R - COOR' -)_n + H_2O$

Note: Some of the R groups contain the reactive ethylenic linkage.

RESIN

PA + MA + PG = Base Resin (Solid)

Base Resin + Styrene = Polyester Resin (liquid)

FIGURE III–29 TYPICAL REACTION AND RAW MATERIALS USED TO FORM UNSATURATED POLYESTER RESIN

reaction mixture. In the second technique, which is referred to as the solvent or azeotropic process, a solvent (usually xylene or toluene) is added to the reaction mixture and forms a constant boiling azeotrope with the water of reaction. This azeotrope is distilled off during the esterification reaction and the solvent is recovered.

After carrying the polymerization reaction to the desired molecular weight and removing the water of reaction, the polymer is transferred to another vessel containing the reactive monomer which is typically styrene, although methyl methacrylate and vinyl toluene are sometimes used. After mixing in the thinning tank, the final composition containing reactive monomer is either discharged to a filtration press prior to being loaded into 208.2 l. (55 gal.) drums or bulk tanks. Discharge from the thinning tank is sometimes carried directly to drums or bulk without filtration. The concentration of reactive monomer can vary considerably (from 20 to about 55 percent by weight). A typical formulation contains about 35 percent styrene.

Although the vast majority of polyester reactions are carried out in batch reactors, there are several plants in the U.S. which have continuous esterification reactors. This mode of operation can usually only be justified when a large quantity of a specific type of polyester resin is desired. The continuous reactor undoubtedly generates less waste per pound of product as compared to batchwise production due to more infrequent cleanout, more efficient operation, and more careful control of operating parameters.

Waste Water Generation - In addition to boiler and cooling tower blowdown, the sources of effluent are as follows:

Water of Reaction

The water of reaction which is passed out overhead is condensed by some means and is either removed directly from the condenser, or more typically from the decanter following the condenser. This condenser also serves as a means for separating the solvents used in azeotropic distillation and sending them back to the reactor. The water of reaction may contain a variety of contaminants, including glycols, acids, and minor quantities of dissolved solvent.

Scrubber Waste

Scrubbers are used on the overheads leaving the reactor in order to reduce the concentration of entrained liquids and solids. Both recirculating and once-through scrubbers are used. The scrubber operation usually consists of passing the gaseous stream leaving the top of the reactor through a column into which water is sprayed. The scrubber may either use a recirculating water stream or once-through water. In the latter case, although the water use is quite high, the effluent concentration in the water stream leaving the scrubber is not high and the stream can therefore be passed to a treatment system. In the case of a recirculating scrubber, however, the BOD and COD concentration can often be 200,000 to 400,000 ppm. Such high concentrations could upset the operation of conventional biological or municipal waste treatment plants, and therefore it is common practice in the industry to either discharge such concentrated recirculating scrubber wastes to a landfill or to incinerate the wastes.

Caustic Cleanout of Reactors

Concentrated caustic solution is typically used to clean out the polymerization reactors. The frequency of reactor cleanout is highly variable depending on the grades and types of resin produced by the manufacturer. Cleanout periods ranging from once every three weeks to once a year were encountered during our interviews. The caustic solution is also used to clean out tank cars and tank trucks. Generally, some form of recycling is practiced on this caustic cleanout solution.

Alkyd Resins - Although there are some notable exceptions, most polyester resin plants also manufacture the alkyd resins which are used in paint manufacture. These resins are quite similar to polyester resins with the exception that the acid portion of the polymerization recipe contains a significant quantity of a long chain of unsaturated fatty acid, and the polymerized resin instead of being diluted with a reactive monomer such as styrene is diluted with a solvent such as xylene or naptha.

With these two exceptions, the processes used to manufacture alkyd resins are quite similar to those used for manufacturing unsaturated polyester resins. Both azeotropic and fusion cook processes are used for manufacturing alkyd resins and, in many cases, identical reactors are used.

The nature of the effluents in alkyd resin and unsaturated polyester resin manufacture is also quite similar, with the notable exception of an increased amount of an oily material which originates from the long chain, unsaturated fatty acids used in the alkyd recipe. The presence of this material often appears as a high "oil and grease" analysis in the discharge. It is also worthy to note that although a typical polyester reaction gives off about 12 percent of the original weight of the reactants as water of reaction, the alkyds, because of the high molecular weight of the reactant, typically give off 5 percent of the weight of the original reactants as water of reaction.

Litharge (lead oxide) and other catalysts such as lithium compounds are often used as alcoholysis catalysts in the reaction vessel in concentrations of a few ppm. Occasionally benzene sulfonic acid is used as an esterification catalyst. Most of these catalysts go out with the polymer or are trapped in the filtration step.

Various additives are often mixed with the resin in the thinning tank. These are color stabilizers such as triphenyl phosphate, amines, fire retardants such as chlorophthalic anhydride, curing accelerators such as cobalt naphthenate, and thixotropic agents such as Cab-o-Sil(R). All these components appear to go out with the resin.

Discharge to municipal waste is the waste treatment method utilized by 90 percent of the polyester/alkyd resin industry. There are some notable exceptions, however, who carry out their own biological treatment or who truck all of the wastes to a large, centralized municipal treatment plant. The exact nature of the wastes can be highly variable depending on such factors as:

- o The use of once-through vs. recirculating scrubbers.
- o The extent to which cooling water is recycled.
- o The frequency of reactor washout.
- o The product mix (polyesters vs. alkyds).
- o Whether or not polymerization catalysts are used.
- o Whether or not wastes are incinerated (41).

Polyimides

The development of thermally-stable polymers has for many years been one of the important tasks in the chemistry of high molecular compounds. Such polymers ideally combine the properties of heat resistance and thermal stability. One of the greatest successes in this direction was the synthesis of polyimides -cyclic chain polymers with the structure shown in Figure III-30, Equation 1. The greatest heat resistance and thermal stability was obtained by the production of completely cyclic polymers with no aliphatic units in the chain.

Polyimides may be divided into two broad groups according to their structure and method of preparation: (1) polyimides with aliphatic units in the main chain; and (2) polyimides with aromatic units in the main chain. Polyimides containing aliphatic units in their main chains of the general formula shown in Figure III-30, Equation 2, are obtained by thermal poly-condensation by heating salts of aromatic tetracarboxylic acids and aliphatic diamines. The preparation of an aliphatic polyimide in this manner is that illustrated in Figure III-30, Equation 3. After heating at 110-138°C (230-280°F), an intermediate low molecular weight product (salt) is formed. This is converted into the polyimide by additional heating at 250-300°C (482-572°F) for several hours.

The melt polycondensation method for the preparation of polyimides has limited applicability. The melting points of the polyimides obtained must be below the reaction temperature so that the reaction mixture will be in the fused state during the polycondensation process. Only in this case is it possible to achieve a high molecular weight. Melt polycondensation can therefore be used successfully only for aliphatic diamines containing at least 7 methylene groups. Aromatic polyimides are generally infusable, so that when aromatic diamines are used, the reaction mixture solidifies too early to permit the formation of a high molecular weight product. Furthermore, aromatic diamines are not basic enough to form salts with carboxylic acid.

Polyimides with aromatic units in the main chain (of the general formula shown in Equation 4, Figure III-30) are generally synthesized by a two-stage poly-condensation method. This method has recently found very widespread use, since soluble products are obtainable in the first stage of the reaction. This first stage, carried out in a polar solvent, consists of the acylation of a diamine by a dianhydride of a tetracarboxylic acid, leading to the

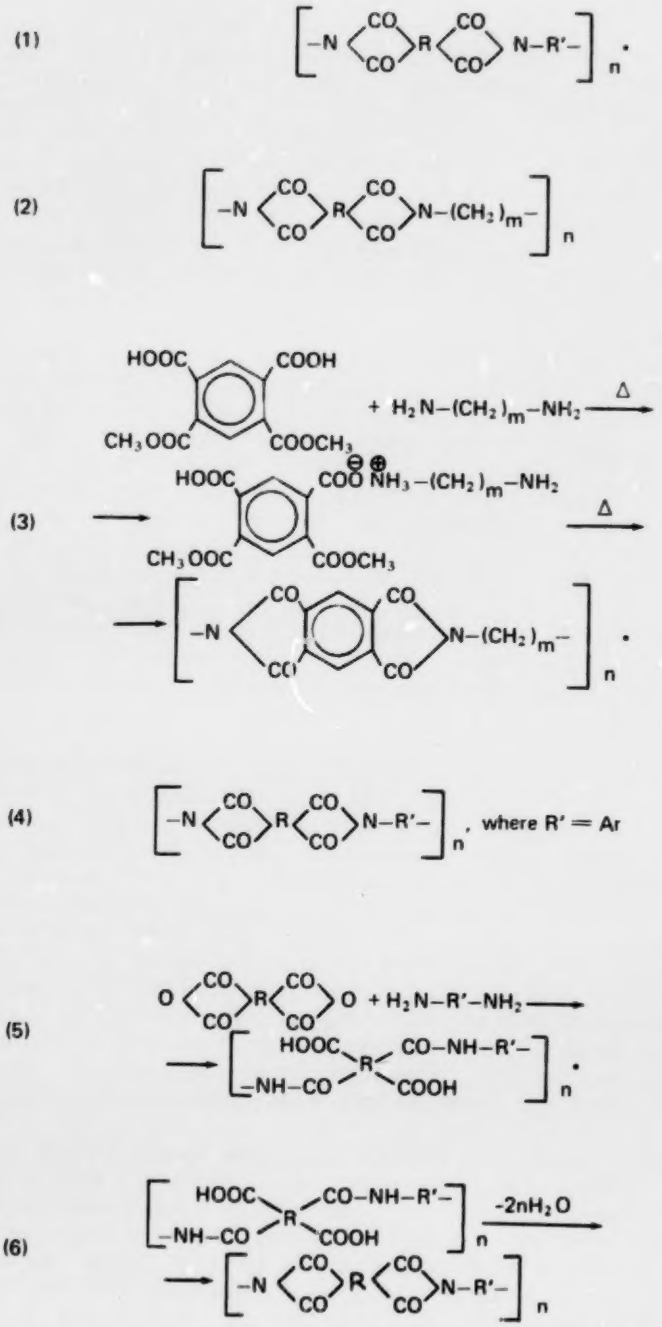

(1)
(2)
(3)
Δ
Δ
(4)
where R' = Ar
(5)
(6)
-2nH₂O

FIGURE III-30 TYPICAL REACTIONS TO FORM POLYIMIDES

formation of a polyamic acid according to Equation 5 of Figure III-30. The second stage of the reaction -- the dehydrocyclization of the polyamic acid (imidization) -- proceeds according to Equation 6, and is carried out thermally or chemically.

The first stage of the synthesis of polyimides -- the preparation of polyamic acid -- is effected as follows. To a solution of an aromatic diamine in a suitable solvent there is added in small portions, with agitation, an equimolar quantity or a slight excess of the dry tetracarboxylic dianhydride. The reaction is carried out at temperatures of -20-70°C (-4-158°F), with the optimum reaction temperature in most cases being 15-20°C (59-68°F). The reaction is carried out in polar solvents, the best of which are N,Ndimethylacetamide, N,N-dimethylformamide, dimethylsulfoxide, and N-methyl-2-pyrrolidone. The polyamic acids as a rule apparently have a low molecular weight (below 100,000) and a low degree of polymerization (140 or lower).

The conversion of polyamic acids to polyimides, imidization, consists of the intramolecular evolution of water from the polyamic acid to form a cyclic polyimide. The imidization reaction can be carried out in two ways, thermally or chemically. The thermal imidization generally consists of heating the dried polyamic acid with a continuous or stepwise increase of temperature. Thermal treatment at high temperatures (above 200°C or 392°F) is carried out in vacuum or an inert medium.

The chemical imidization method consists of a treatment of polyamic acid film or powder with dehydrating agents. Acetic anhydride or anhydrides of other lower aliphatic acids, such as propionic acid, can be used for this purpose.

Most polyimides, particularly the thermally stable aromatic polyimides which are of great practical significance, are inert toward organic solvents and oils. They are also little affected by dilute acids, but dissolve in strong acids such as fuming nitric or concentrated sulfuric acid. Polyimides have a relatively low stability toward alkalis and superheated steam, and under the action of both they are hydrolyzed.

Polyimides have been used as electrical insulating films, for wire enamel, for testing compounds, and for adhesives. They are being produced for the most part on a semi-industrial scale.

Polyimide Films - The compounds of primary industrial significance are the aromatic polyimides. The DuPont Company started the production of polyimide film in experimental quantities in 1962. At the present time this company is producing two types of film under the general trademark Kapton: H-Film made from the pure polyimide, and H-F-Film made from the polyimide and coated on one or both sides with Teflon.

The main area for application of polyimide film at this time is as a heat resistant insulating, gasketing, and winding material for electric machines, and also for electric cables. The use of polyimide films for flexible printed circuits is of great interest. Thin polyimide film can be used for condenser insulation for operating temperatures up to 250°C (482°F).

Polyimide Plastics - Production of polyimide plastics, in which all advantages of these polymers are completely realized, involves greater technological problems than the production of films. The difficulties are caused primarily by the necessity for the removal of large quantities of salt. Polyamic acid solutions generally contain no more than 20-30 percent of dry material. In addition, the water of imidization must be removed. The direct conversion of a concentrated polyamic acid solution into a polyimide block in a manner similar to that used for epoxy resins has not been achieved so far. The preparation of polyamic plastics, therefore, generally requires isolation of the polyamic acid from solution in the form of thin films, powders, coatings on glass, tape, or the like, followed by complete or partial imidization of these intermediate products by a chemical or thermal method. Processing into articles by molding, sintering, or other methods then follows.

Actual consumption of polyimides for the period since 1970 are not known. However, prior to 1970 one estimate predicted a meteoric rise in consumption of polyimides rising to 50 million pounds per year by 1972 or 1973.

Manufacture - Specific information on manufacturing processes has not been reported in the literature, probably for proprietary reasons in this relatively new field. Patents largely refer to bench-scale syntheses, as described previously.

Waste Water Generation - The generation of water wastes during polyimide manufacture is not documented. The general synthesis of interest, that represented by Equations 5 and 6 in Figure III-30, leads to the generation of two moles of water per mole of imide linkages. If R and R' refer to phenyl groups, then this corresponds to generation of 125 mass units of water per 1000 mass units of polymer products.

In this two-stage polycondensation reaction, water is either removed thermally in the vapor state under vacuum, or chemically through the use of dehydrating agents. In the former case, the water may be quite pure when condensed. In the latter case, the condition of the effluent water will depend upon the method of regeneration of the dehydrating agent.

The melt polycondensation method is now obsolete for most purposes. However, it is worth noting that this polymerization and related polymerization methods lead to the release of two moles of methanol per mole of imide linkage (25).

Polymethyl Pentene

Methyl pentene (or 4-methyl-1-pentene) is made by the alkali metal catalyzed dimerization of propylene as shown in Equation 1 of Figure III-31. The polymerization of 4-methyl-1-pentene to produce poly(methyl pentene) can be carried out with ZieglerNatta catalysts in inert hydrocarbon diluents such as cyclohexane, heptane, and commercial saturated aliphatic hydrocarbon fractions. It can also be homopolymerized in bulk. The polymerization reaction is shown in Equation 2 of Figure III-31. The typical polymerization product contains a mixture of the crystalline isotactic polymer (which is almost insoluble in warm aliphatic hydrocarbons) and an amorphous, atactic polymer which is soluble in the diluent. The relative proportion of these two products in the polymer mix depends on such factors as the type of transition metal-halide catalyst plus organometallic activator used and the temperature of polymerization (high temperatures favor the formation of atactic polymer). The catalyst most frequently used is based on titanium trichloride activated by diethyl aluminum chloride.

In a typical polymerization, the diluent serves as a solvent for monomer, activator, and the atactic product which is carried out in the temperature range of 20-80°C (68-176°F). The titanium trichloride and the isotactic polymer remain insoluble. Thus, the monomer polymerizes at the titanium trichloride-liquid interface, and the isotactic polymer precipitates out on the TiCl# crystals forming a slurry of catalyst-polymer particles in the diluent. To isolate the isotactic polymer, the slurry of catalyst-isotactic polymer particles in the diluent is treated with agents which kill the catalyst activity and solubilize the catalyst residues so that they can be washed out. An alcohol is usually employed for this purpose. The polymer is separated from the wash liquors by filtration or centrifugation. Residual liquor held in the polymer particles can then be removed by steam distillation and/or drying. An important feature of the 4-methyl-1-pentene polymer is its optical clarity which can only be attained by the almost complete removal of catalyst residues. In order to obtain this high degree of catalyst residue removal, aqueous washings (as used in polypropylene manufacture) are inadequate, and more complex systems involving washing with hydrocarbons or with alcohols are required.

Waste Water Generation - The waste water generation occurs during washing, and solid/liquid separations since the polymerization reaction does not produce water. The polymer

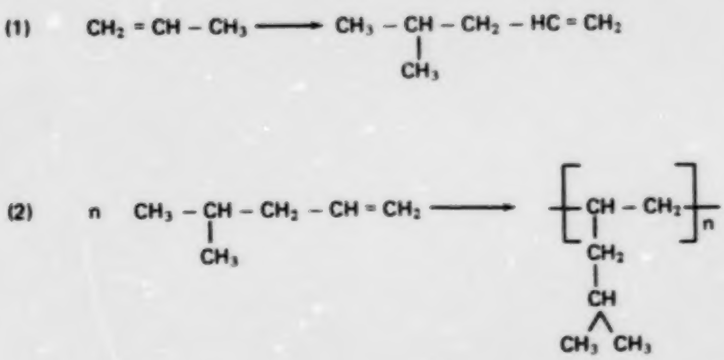


FIGURE III–31 TYPICAL REACTIONS TO FORM POLYMETHYL PENTENE

washing step may use water or, in some cases, hydrocarbon or alcohol. Consequently, the wash liquids may contain dissolved metals. The volume of waste waters per unit of production is expected to vary widely depending upon the specific operations, and the waste waters may also contain hydrocarbons or alcohols from other washing operations (25).

Polyphenylene Sulfide

Polyphenylene sulfide polymers possess recurring units of sulfur which provide linkage for aromatic compounds. Polyphenylene sulfide (PPS) is a finely divided light-colored powder and is insoluble in any known solvent below 190°C (375°F). Above this temperature it has limited solubility in some aromatic and chlorinated aromatic solvents and certain heterocyclic compounds. It is highly crystalline with a melting point near 285°C (550°F). Although curing in air at elevated temperatures is required to effect chain extension and crosslinking, the resin remains thermoplastic in nature. It can be processed through conventional equipment for compression and injection molding.

Polyphenylene sulfide is a recent thermoplastic on the market; therefore only a small amount of information on its synthesis is available in the literature. It is believed that the process employs p-dichlorobenzene, sodium sulfide, and polar organic material such as n-methyl pyrrolidone to yield PPS which may or may not have crosslinking agents added to the reaction medium.

P-dichlorobenzene is solid with a melting point of 53.1°C (127.5°F), a specific gravity of 1.46, and is insoluble in water. Sodium sulfide in the hydrated form contains 9 moles of water and is very soluble in water. N-methyl pyrrolidone is a liquid which boils at 197°C (387°F) and is soluble in water.

The reaction between the two raw materials takes place in the presence of a polar organic solvent as shown in Figure III-32.

The reaction is carried out at a temperature in the range of 130-175°C (266-347°F). The mole ratio of p-dichlorobenzene to sodium sulfide should be in the range of 0.9:1 to 1.3:1. If ratios above this range are employed, the amount of unreacted dichlorobenzene will be increased, requiring separation and recycle. Larger excess of either reagent leads to lower molecular weight polymers, and still shorter polymers are produced by an increase in the reaction temperature.

In general, the synthesis reaction is carried out by reacting a polyhalo-substituted compound with an alkali metal sulfide which has been partially dehydrated by the polar organic compound that also serves as the solvent for the reactants. The solvent should be stable at the elevated temperatures for the reaction. The polymer formed may be

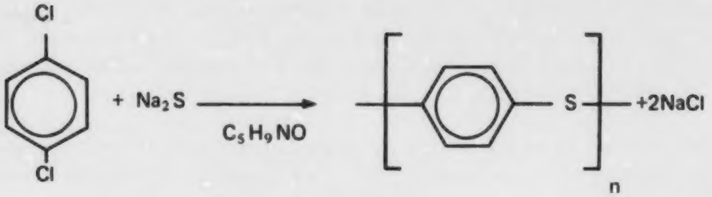

Cl
+ Na₂S
C₅H₉NO
Cl
S
+2NaCl
n

FIGURE III–32 TYPICAL REACTION TO FORM POLYPHENYLENE SULFIDE

heat treated in the absence of oyxgen to yield a higher molecular weight polymer. Molecular weight control may be achieved by introducing a monohalo-substituted aromatic compound to the reaction medium, which causes termination of the chain growth. Yields of finished polymer are higher if a catalyst such as copper or a copper compound is added to the reaction medium.

It is possible to obtain a cross-linked polymer through addition of a polyhalo-substituted aromatic compound which contains substituents through which crosslinking can be effected by further reaction.

Manufacture - A typical process scheme is shown in Figure III-33.

The hydrated sodium sulfide in n-methyl-pyrrolidone is charged to a stainless steel autoclave. The temperature is brought up to 190°C (374°F) while flushing with nitrogen to remove the water of hydration. Upon removal of water, the p-dichlorobenzene is charged to the autoclave and the temperature raised to approximately 250°C (482°F) for the desired reaction time after which the polymer and reaction medium is dropped to a stainless steel tank. The contents are washed with water and then with acetone, which carries along unreacted reaction media. The finished polymer is dried and packaged.

Waste water Generation - Aqueous wastes would be generated from two sources:

1. Water of hydration.

2. Process wash water. The primary contaminant would be sodium chloride, of which two moles would be generated per mole of feedstock.

The water of hydration is associated with the water bound to the sodium sulfide which is removed in a pre-reaction step by heating. It is likely that the water removal would carry along traces of sodium sulfide and n-methyl pyrrolidone which may or may not be recovered. Process wash water is used to wash sodium chloride from the reaction mass. Due to the high solubility of n-methyl-pyrrolidone and sodium sulfide in water, the waste generated from this source is most apt to contain a large waste loading. It is likely that solvent extraction and subsequent further recovery operations will be applied to this stream to recover the raw materials for recycle.

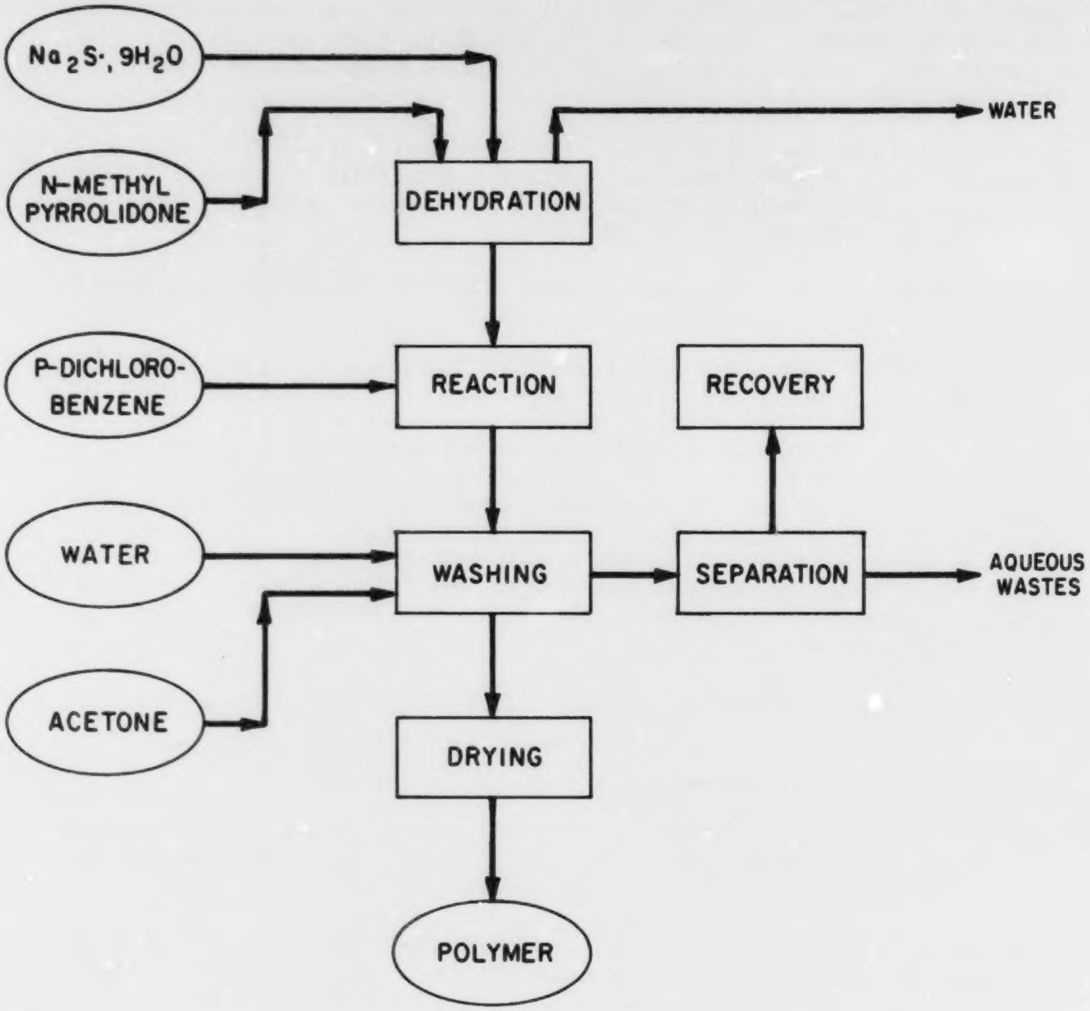

$Na_2S\cdot, 9H_2O$
N-METHYL PYRROLIDONE
DEHYDRATION
WATER
P-DICHLOROBENZENE
REACTION
RECOVERY
WATER
WASHING
SEPARATION
AQUEOUS WASTES
ACETONE
DRYING
POLYMER

FIGURE III-33 POLYPHENYLENE SULFIDE PRODUCTION

If it is assumed that the sodium chloride is removed in a water solution at a concentration of about 10 percent by weight, then about 10,000 mass units of water per 1,000 mass units of product would be required (24, 47).

Polypropylene Fibers

Manufacture - The polymerization of polypropylene was described previously in EPA Development Document No. EPA 440/1-73/010 ±161. Polypropylene fibers are made by melt spinning. The general process, shown in Figure III-34, consists of coloring polypropylene flake by some type of dry blending of the flake with pigments followed by a melting and extrusion process that regenerates the colored polypropylene as pellets. The pellets are then extruded through a spinnerette into a column of air which solidifies the molten filaments. The filaments are subsequently stretched or spun and crimped, depending on the applications of the final fiber.

As in most melt-spun fibers, drawing is the critical step in fiber manufacture. The quenched filaments are heated and drawn to develop molecular orientation along the fiber axis. To relieve internal stresses and provide dimensional stability, the filaments are heat set. This last step also aids in development of a higher degree of crystallinity. Fibers with degrees of crystallinity of about 70 percent can be obtained under optimum quenching and annealing conditions.

There are three basic types of polypropylene filaments. These include monofilaments, which may be round or flat or have special cross-section; fibers; and fibrillated or slit film.

Monofilaments

A typical extrusion and orientation arrangement for monofilament is shown in Figure III-35, in which can be seen that extruded filaments coming from the spinnerette are quenched in a water bath (quench tank) and then hot stretched to several times their original length between a series of heated Godet rolls and ovens. The source of heat can be hot water, steam or hot air. After leaving the orientation oven, the filaments must then be annealed by heating to a specific temperature (heat set temperature) while maintaining an essentially constant length but permitting a limited amount of retraction. This procedure stabilizes the filament against shrinkage up to the heat set temperature.

Fibers

Polypropylene fibers are produced from 1-1/2 denier up to about 15 denier by a technique basically resembling

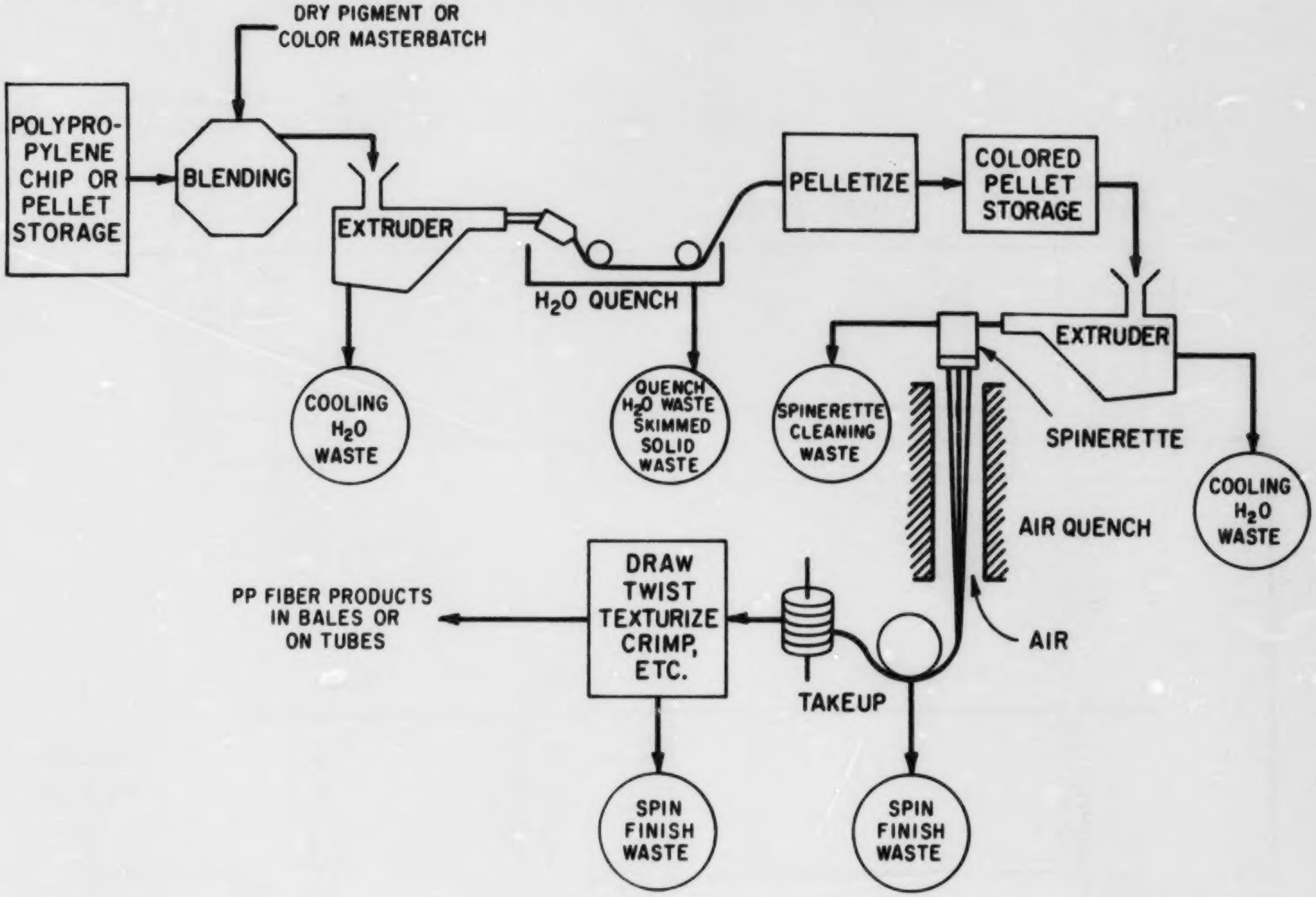
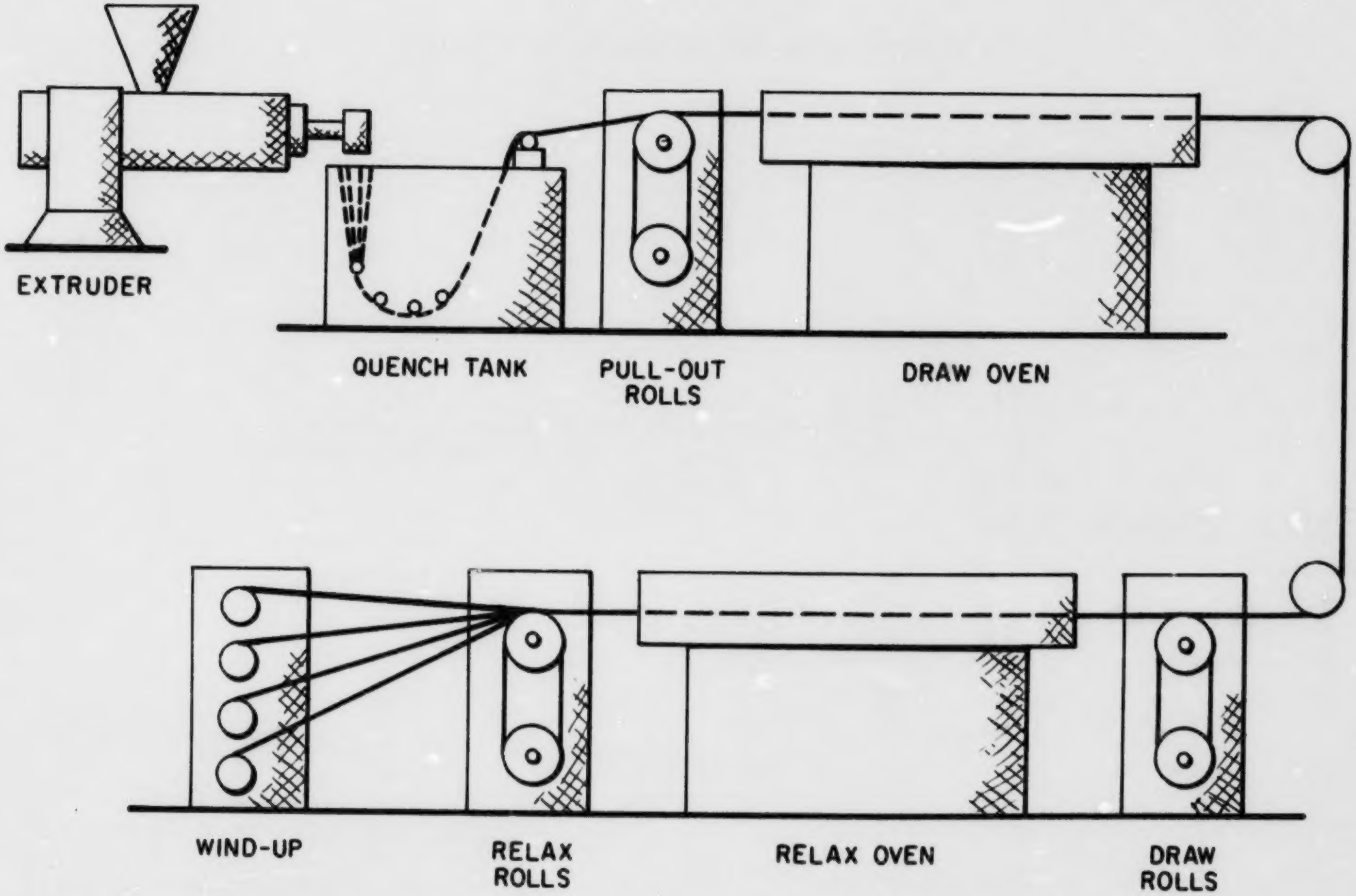

DRY PIGMENT OR COLOR MASTERBATCH
POLYPROPYLENE CHIP OR PELLET STORAGE
BLENDING
EXTRUDER
COOLING H_2O WASTE
H_2O QUENCH
QUENCH H_2O WASTE SKIMMED SOLID WASTE
PELLETIZE
COLORED PELLET STORAGE
EXTRUDER
COOLING H_2O WASTE
SPINERETTE CLEANING WASTE
SPINERETTE
AIR QUENCH
AIR
TAKEUP
SPIN FINISH WASTE
DRAW TWIST TEXTURIZE CRIMP, ETC.
SPIN FINISH WASTE
PP FIBER PRODUCTS IN BALES OR ON TUBES

FIGURE III-34 POLYPROPYLENE FIBER PRODUCTION


EXTRUDER
QUENCH TANK
PULL-OUT ROLLS
DRAW OVEN
WIND-UP
RELAX ROLLS
RELAX OVEN
DRAW ROLLS

SOURCE: POLYPROPYLENE FIBERS AND FILMS, A.U. GALANTI and C.C. MANTELL, PLENUM PRESS, NEW YORK (1965).

FIGURE III-35 POLYPROPYLENE MONOFILAMENT PRODUCTION

that used for nylon and polyester fibers. After extruding the filaments downward and quenching by air under carefully controlled conditions, the now undrawn filaments are collected on bobbins in bundles and then passed to the stretching operation. There are two different methods of stretching depending on the desired end product: one for continuous multifilament yarn and another for staple fiber. For continuous multifilament yarn, the bundles are removed from the individual bobbins and are drawn under heat to four to eight times their original length (stretch ratios of 1:4 to 1:8). Typical drawing equipment consists of heated metal shoe over which the bundles are run; occasionally steam or hot air heating is used.

In many cases the multifilament is used in the form of a twisted yarn. This is made in a draw twister, which combines a twisting motion with the stretching operation.

Staple fiber is produced from tow containing several hundred thousand filaments which are combined from creels. These tows are usually stretched in successive steps to stretch ratios of 1:3 or 1:4. After drawing, the tow is normally crimped (or deformed) by heat using specially shaped rollers to give bulk to the fiber (approximately that of wool, for example). The crimped tow is then cut to staple fiber in lengths ranging from 1.3-12.7 cm (1/2-5 in.).

Fibrillated or Slit Film

This product is made by extruding or casting the polypropylene into a thin film, which is then stretched to obtain a high degree of orientation of the crystalline structure. This highly-oriented film is then fibrillated by applying various kinds of forces perpendicular to the machine direction. The fibrillation splits the sheet into fibers which are then processed into the final product.

Slit film is made in a similar manner with the exception that the extruded film is slit into thin widths prior to the stretching step. In making slit film, lower stretch ratios are used in order to avoid fibrillating the film.

The applications of polypropylene fiber include carpet face yarns, carpet backing, and various industrial yarn applications.

Waste Water Generation - Water is used as a heat exchange medium in the extruders and in the air conditioning system of the plant. Water is also used as a rinsing medium for various equipment and kettles associated with the blending step.

Sources of waste include rinse water from the blending step, extensive quantities of cooling and air conditioning water, and the spin and crimping finish waste. These are lubricants that will contribute to an oil and grease analysis. The crimping finish wastes are sometimes directly drummed and sent to landfill rather than being put into the waste water stream because of their high BOD's. Some dissolved solids are generated by the rinsing of gear pump parts that are periodically removed from service and cleaned in a molten salt bath. In common with other fiber production plants, polypropylene plants have a large number of employees due to the number of hand operations associated with the handling of the product, and therefore sanitary wastes account for a significant portion of the total effluent load from the plants (41). Phosphate can be present in the wastes due to phosphate containing surfactants.

Polysulfone Resins

Polysulfones are high-molecular-weight polymers containing sulfone groups and aromatic nuclei in the main polymer chain. The term "polysulfone" is also used to denote the class of polymers prepared by radical-induced copolymerization of olefins and sulfur dioxide. The latter do not have commercial significance, and will not be discussed.

Among the aromatic polysulfones synthesized, the polysulfone derived from dihydric phenols (bisphenol A) and 4,4'-dichlorodiphenyl sulfone have achieved commercial application under the trade name of Bakelite polysulfone. This is a rigid, strong thermoplastic which can be molded, extruded, or thermoformed into a variety of shapes. It is both stable and self-extinguishing in its natural form. Bakelite (R) polysulfone is prepared from the two raw materials under alkaline conditions according to the equations listed in Figure III-36, Equations 1 and 2.

The disodium salt is prepared in situ by reaction of bisphenol A with exactly two moles of aqueous sodium hydroxide. A solvent is required for this polymerization, dimethyl sulfoxide being the most suitable. Very few others are effective. The reaction must be carried out at 130-160°C (266-320°F), primarily because of the poor solubility of the disodium salt at lower temperatures. Polymerization is, however, very rapid at these temperatures, leading to molecular weights as high as 250,000 in an hour's time. As these molecular weights are too high for commercial processing, chain growth must be regulated by the addition of terminators. A variety of monohydric phenolic salts or monohalogen compounds have been found to be effective.

In the polymerization, the highest molecular weights will be obtained when the mole ratio of co-monomers approaches unity. Since the co-monomers contain two functional groups per molecule, as is required for this type of polycondensation, addition of a compound containing one functional group per molecule will result in an overall imbalance in functionality, terminating chain growth.

All but traces of water must be removed from the reaction mixture before polymerization. Hydrolysis of the dihydric phenol salt occurs otherwise, resulting in the formation of sodium hydroxide, which reacts very rapidly with the dichlorodiphenyl sulfone, forming the monosodium salt of 4-chloro-4'-hydroxydiphenyl sulfone (Figure III-36, Equation 3).

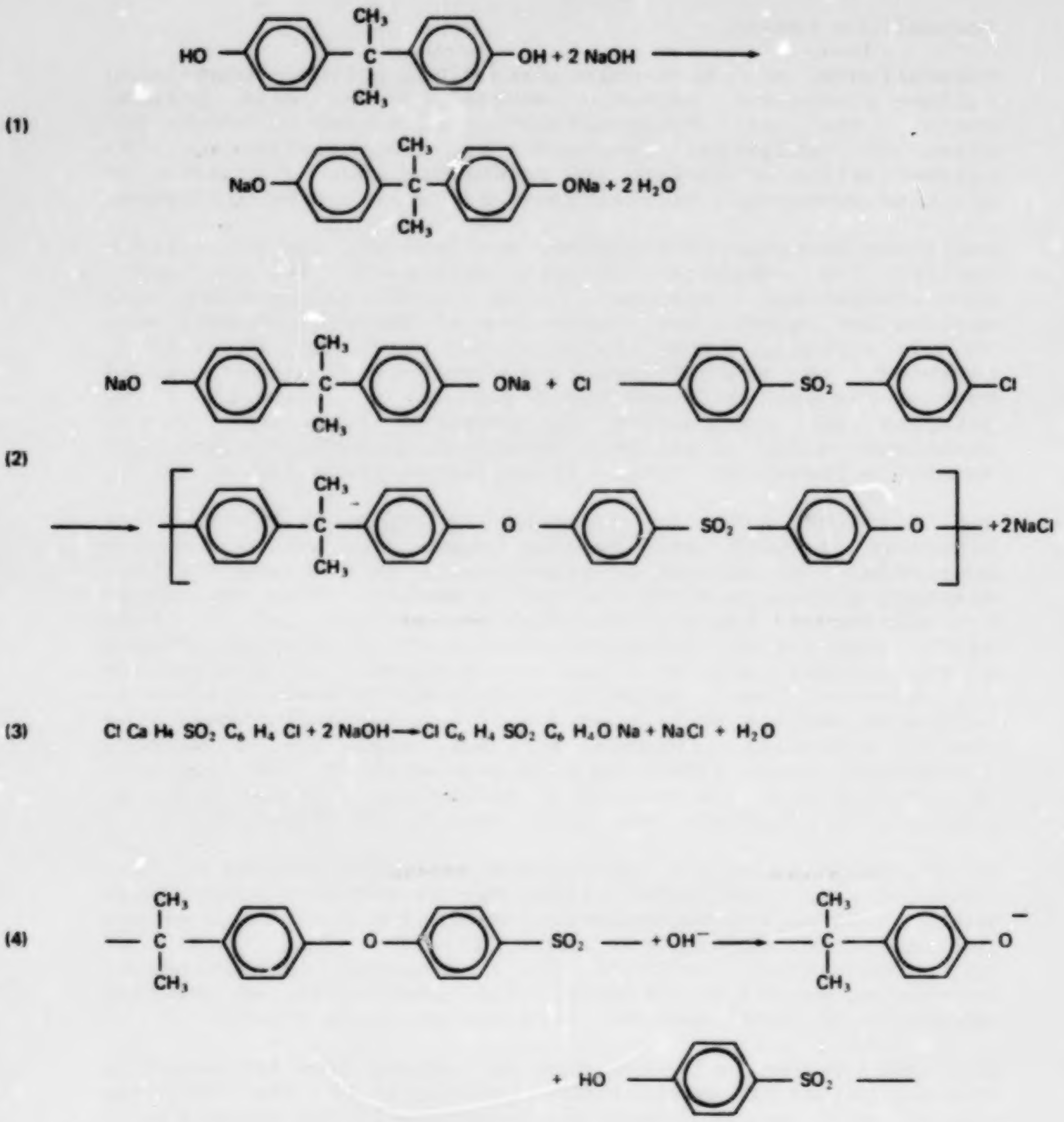

(1)
HO
CH₃
C
CH₃
OH + 2 NaOH
NaO
ONa + 2 H₂O
(2)
ONa + Cl
SO₂
Cl
O
+2NaCl
(3)
Cl Ca H₄ SO₂ C₆ H₄ Cl + 2 NaOH → Cl C₆ H₄ SO₂ C₆ H₄O Na + NaCl + H₂O
(4)
+ OH⁻
O⁻
+ HO

FIGURE III-36 TYPICAL REACTIONS TO FORM POLYSULFONE RESINS

Two moles of caustic soda (from 2 moles of disodium salt) are used per mole of dichlorodiphenyl sulfone, which creates an imbalance in functionality between the co-monomers. Consequently, it becomes impossible to obtain high molecular weight.

Another, somewhat less important, side reaction may occur if caustic soda is present during polymerization. Cleavage of polymer chains para to the sulfone groups results in the formation of two phenoxides, as shown in Figure III-36, Equation 4, for polysulfone.

Other bisphenol A-derived polysulfones are prepared by using various combinations of dihydric phenol sodium or potassium salts and dichlorodiphenyl sulfone. Use of certain other aromatic dihalides besides dichlorodiphenyl sulfone expands the list considerably.

Manufacture - A typical process scheme is shown in Figure III-37. Polymerization of bisphenol A and 4,4'-dichlorodiphenyl sulfone (DCDPS) is carried out batch-wise by first forming the disodium salt of bisphenol A. This is done by charging bisphenol A and an excess of dimethyl sulfoxide (DMSO) to a reactor where the temperature is brought up to 60-80°C (140-176°F). Sodium hydroxide as a 50 percent solution is added stoichiometrically to the mixture over a period of about 10 minutes. Water is removed from the system, the DMSO that co-distills being returned continuously. In so doing, the temperature of the contents rises from about 120°C (248°F) initially to 140°C (284°F) at the conclusion of this step. When this point is reached, most of the water originally present has distilled, and the disodium salt of bisphenol A appears as a precipitate.

Excess azeotrope solvent is distilled from the system until the temperature of the contents reaches 155-160°C (311-320°F). At this point the precipitate will redissolve with the formation of a very viscous solution. It is assumed that at this point only traces of water remain.

A 50 percent solution of 4,4'-dicholordiphenyl sulfone (DCDPS) in DMSO maintained at 110°C (230°F) is fed stoichiometrically to the polymerizer. The temperature must not drop below about 150°C (302°F) until the polymerization is well along, since sodium-ended low polymer may precipitate on the walls of the reactor. Too high a temperature during addition of the sulfone and subsequent polymerization is to be avoided, as the reaction is mildly exothermic, extremely rapid over 160°C (320°F), and

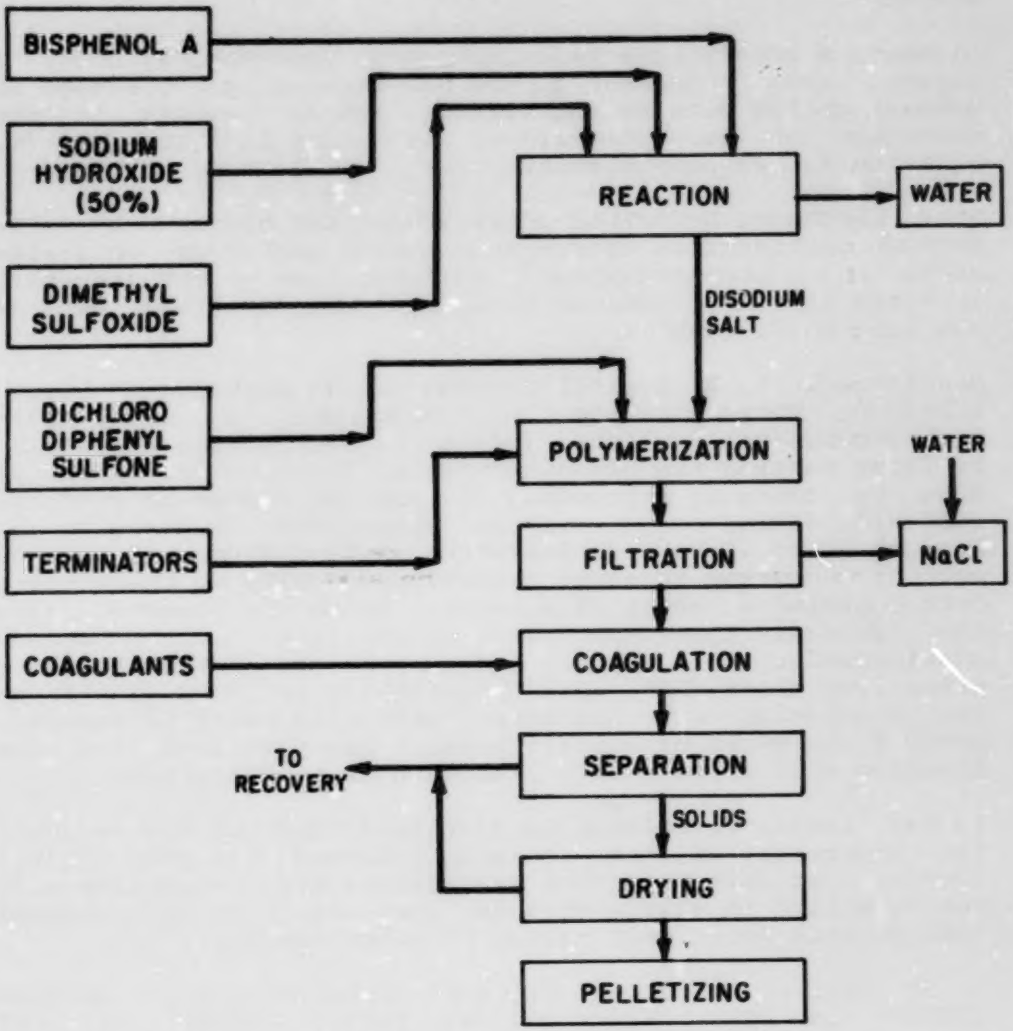

BISPHENOL A
SODIUM HYDROXIDE (50%)
DIMETHYL SULFOXIDE
DICHLORO DIPHENYL SULFONE
TERMINATORS
COAGULANTS
REACTION
WATER
DISODIUM SALT
POLYMERIZATION
WATER
FILTRATION
NaCl
COAGULATION
SEPARATION
TO RECOVERY
SOLIDS
DRYING
PELLETIZING

FIGURE III-37 POLYSULFONE RESINS PRODUCTION

excessive solvent decomposition and/or discoloration or even gelation of the reaction mass may occur.

The polymerization may be terminated in a variety of ways, one of which is to pass methylene chloride into the polymerizing mixture when the desired degree of polymerization is reached.

Additional DMSO is added to the reactant mixture to reduce the viscosity to a workable level. The mixture is then passed through a rotary drum filter to remove sodium chloride. The process stream is fed to a coagulation vessel where an alcohol such as ethanol is added to coagulate the polysulfone. The solvent and unreacted feed materials are separated from the polymer and sent to recovery. The polymer is then dried and pelletized while the vented solvent is recovered and recycled.

Waste Water Generation - The reaction products include 810 mass units of water per 1000 mass units of the disodium salt, and an estimated 1800 mass units of water is added with the sodium hydroxide for a total of 2610. The waste water from the azeotropic distillation are likely to contain DMSO and traces of bisphenol. In addition, appreciable concentrations of sodium chloride are expected to occur. The waste waters are expected to be alkaline because of the excess sodium hydroxide required for pH control. The volume of waste water generated is highly dependent upon operating conditions, especially those associated with the washing operations (25, 27).

Polyvinyl Butyral

Polyvinyl butyral is formed by condensation of polyvinyl alcohol with butyraldehyde in the presence of an acid catalyst (Figure III-38).

Manufacture - Two processes, shown in Figures III-39 and III-40, are used for production of polyvinyl butyral.

The process shown in Figure III-39, which is used by E. I. DuPont de Nemours and Company, Inc., Fayetteville, N.C., starts with powdered polyvinyl alcohol. The alcohol is dissolved in water and reacted with butyraldehyde according to the equation in Figure III-38. The butyral is washed and slurried in water. The slurry is treated with a plasticizer (triethylene glycol di-2-ethyl butyrate is one), and the mixture is sheeted to give the product that is sandwiched and heat sealed between pieces of glass to produce safety glass.

The process shown in Figure III-40 is practiced by Monsanto Co., Indian Orchard, Mass., and Trenton, Michigan. At these plants, vinyl acetate monomer is polymerized in suspension to give polyvinyl acetate. This polymer is separated, dissolved in ethyl alcohol and hydrolyzed in the presence of a mineral acid. The polyvinyl alcohol is centrifuged and condensed with butyraldehyde in the presence of ethyl alcohol and acid. The butyral solution is filtered, precipitated with water, washed and dried.

The dry product may be sold as such, or transferred to another area of the Monsanto plant for sheeting. In this operation, the polymer is combined with plasticizer and sheeted on rolls. The sheeting process uses very little water, and wastes are negligible.

Waste Water Generation - Wastes generated in the DuPont process are indicated in Figure III-39. The acid catalyst, small amounts of the reaction components, and a small amount of the plasticizer are anticipated wastes.

Wastes generated by the Monsanto process, shown in Figure III-40, are considerably more complex than those generated by the DuPont process. The Monsanto process requires ethanol, which is not needed in the DuPont process; the ethanol combines with acetic acid which is liberated in the hydrolysis step to give ethyl acetate, which is recovered (31, 41).

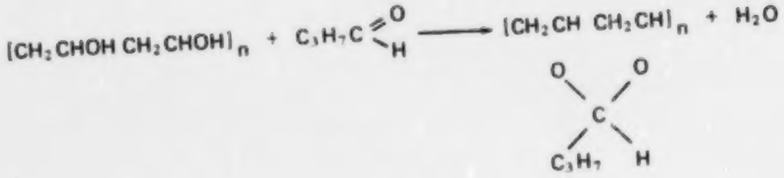
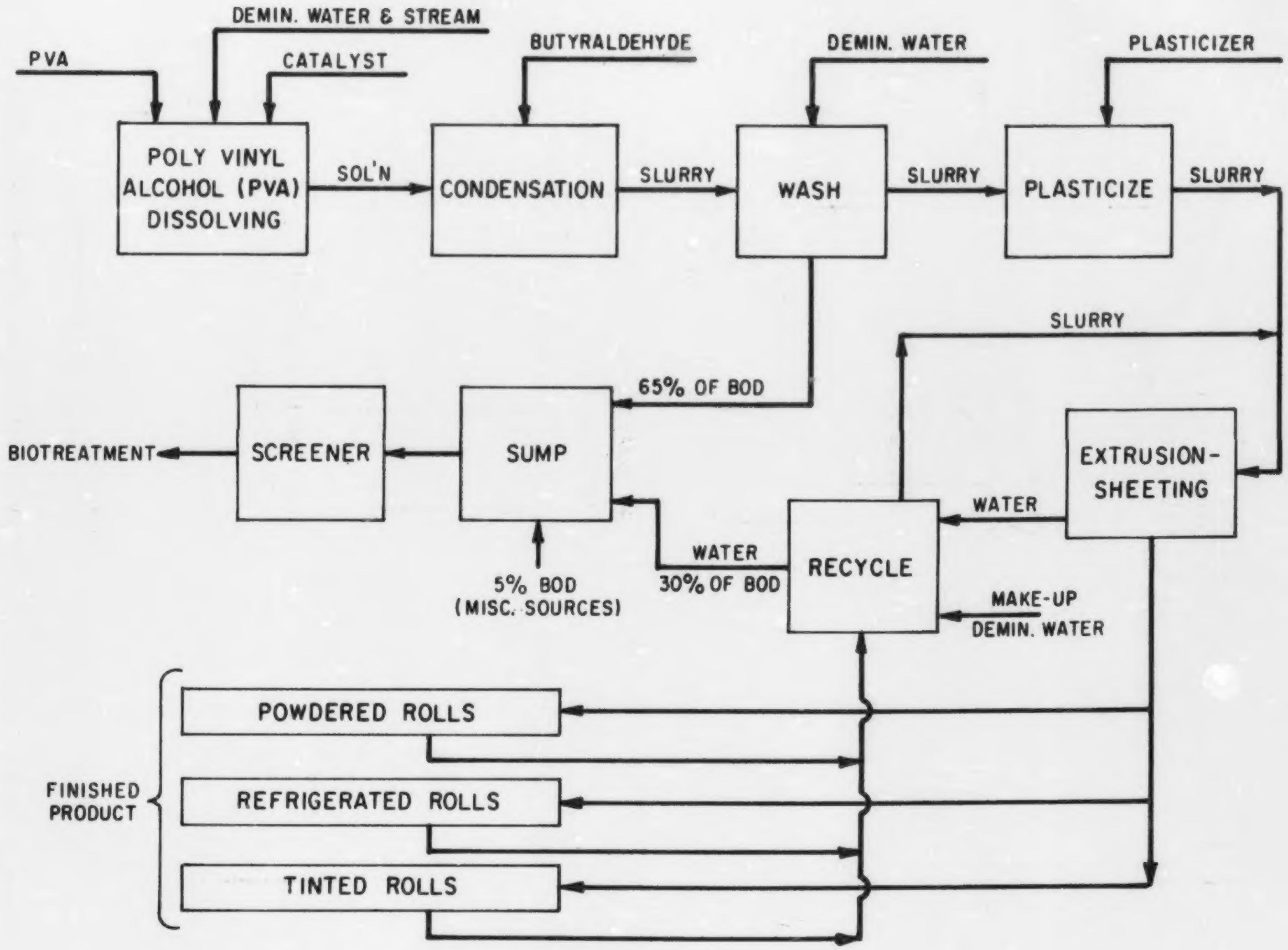


FIGURE III–38 TYPICAL REACTION TO FORM POLYVINYL BUTYRAL



PVA
DEMIN. WATER & STREAM
CATALYST
POLY VINYL ALCOHOL (PVA) DISSOLVING
SOL'N
BUTYRALDEHYDE
CONDENSATION
SLURRY
DEMIN. WATER
WASH
SLURRY
PLASTICIZER
PLASTICIZE
SLURRY
SLURRY
65% OF BOD
EXTRUSION-SHEETING
WATER
BIOTREATMENT
SCREENER
SUMP
WATER
30% OF BOD
RECYCLE
5% BOD (MISC. SOURCES)
MAKE-UP DEMIN. WATER
POWDERED ROLLS
REFRIGERATED ROLLS
TINTED ROLLS
FINISHED PRODUCT

FIGURE III-39 POLYVINYL BUTYRAL PRODUCTION – DU PONT INC. PROCESS

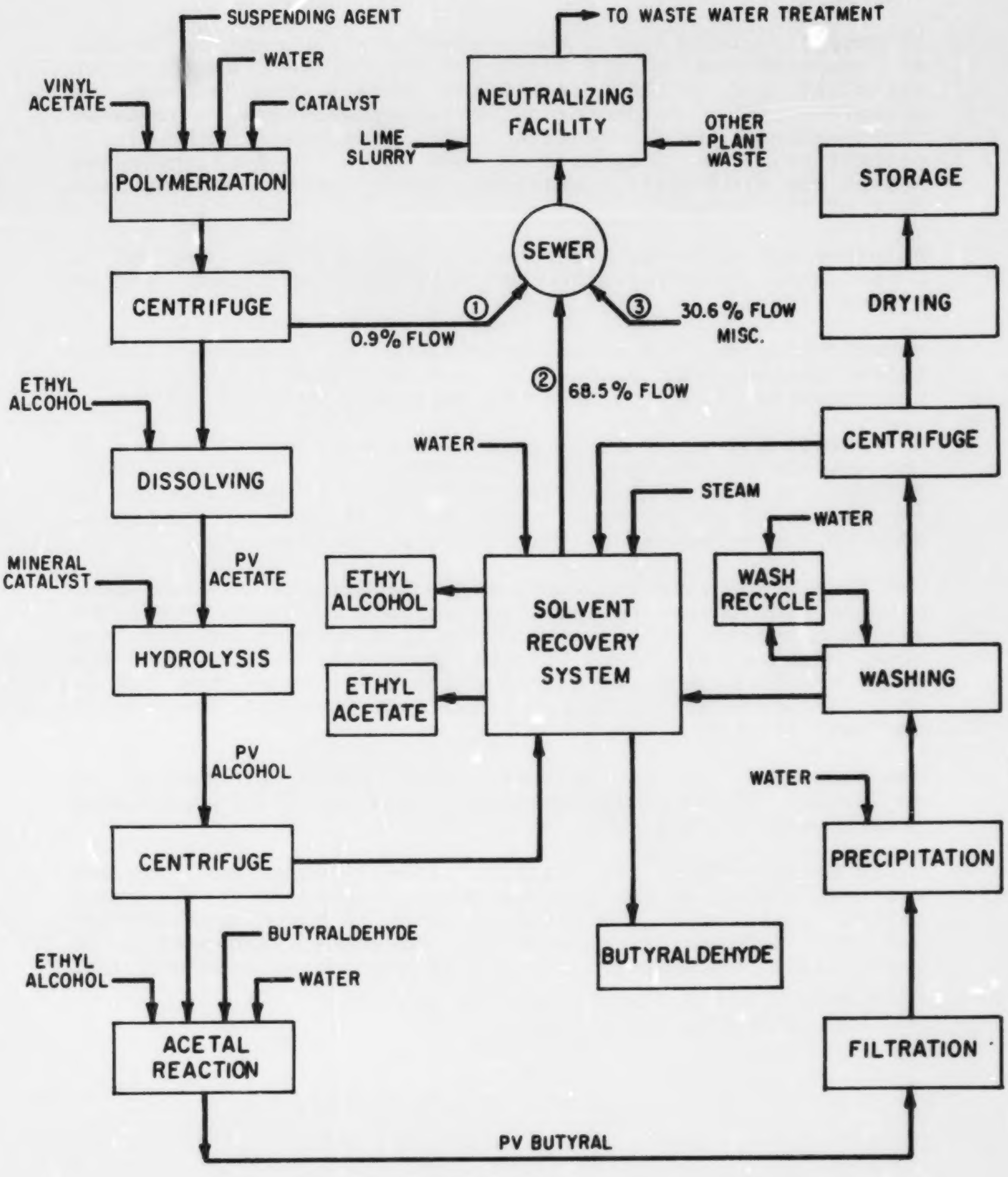

SUSPENDING AGENT
WATER
VINYL ACETATE
CATALYST
POLYMERIZATION
CENTRIFUGE
ETHYL ALCOHOL
DISSOLVING
PV ACETATE
MINERAL CATALYST
HYDROLYSIS
PV ALCOHOL
CENTRIFUGE
BUTYRALDEHYDE
ETHYL ALCOHOL
WATER
ACETAL REACTION
PV BUTYRAL
TO WASTE WATER TREATMENT
NEUTRALIZING FACILITY
LIME SLURRY
OTHER PLANT WASTE
SEWER
①
0.9% FLOW
②
68.5% FLOW
③
30.6% FLOW MISC.
WATER
STEAM
ETHYL ALCOHOL
ETHYL ACETATE
SOLVENT RECOVERY SYSTEM
BUTYRALDEHYDE
STORAGE
DRYING
CENTRIFUGE
WATER
WASH RECYCLE
WASHING
WATER
PRECIPITATION
FILTRATION

FIGURE III-40 POLYVINYL BUTYRAL PRODUCTION – MONSANTO INC. PROCESS

Polyvinyl Carbazole

Polyvinyl carbazole is a thermoplastic which can be molded at temperatures of 210-270°C (410-518°F) into sheets which are clear and stiff, resembling mica. The polymer is soluble in chloroform, trichloroethylene, aromatic hydrocarbons, etc. Despite its excellent dielectric properties, the polymer has not been used to any great extent for electrical insulation, mainly because of the high cost of the monomer.

Poly(N-vinyl carbazole) can be prepared via the use of a Lewis acid catalyst. The polymerization is illustrated in Figure III-41.

Substitution of other solvents such as toluene, carbon tetrachloride, etc., or the use of higher polymerization temperatures, all lead to lower molecular weight products.

Alternatively, very highly purified monomer may be heated in the absence of catalyst at temperatures of 85-120°C (185-248°F), to give a nearly colorless clear product similar in appearance to polystyrene. Even small amounts of impurities lead to low molecular weight products, however.

The literature reports successful polymerization with zinc bromide initiated by passing an electric current. The yields increased with increased applied current density and were high after short times. Molecular weights were low (2000 to 5000), but the distribution was very narrow. It is doubtful that this technique will reach commercialization in the near future.

Manufacture - It is presumed that batch processing is employed. Further information is unavailable in published literature.

Waste Water - While the reaction itself does not produce wastes, washing of the product polymer would produce aqueous wastes containing the catalyst (such as boron trifluoride) and small amounts of the solvent. Adequate information is unavailable to make projections of quantities involved (25, 29).

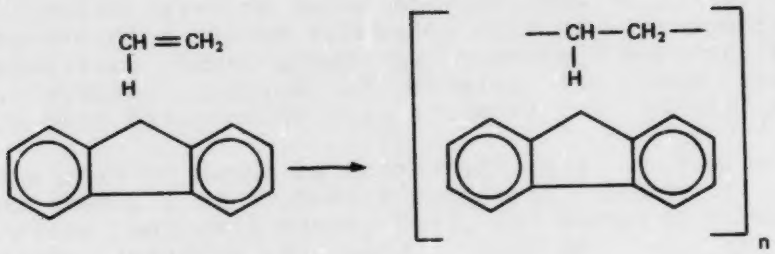

CH = CH₂
H
— CH — CH₂ —
H
n

FIGURE III–41 TYPICAL REACTION TO FORM POLYVINYL CARBAZOLE

Polyvinyl Ethers

The various vinyl alkyl ether monomers (the reactants) are normally colorless liquids or low melting solids. All readily add halogens across their double bonds. The lower alkyl vinyl ethers are sparingly soluble in water. These monomer ethers hydrolyze slowly in water at room temperature (and more rapidly in the presence of mineral acids), producing acetalydehyde, as shown in Figure III-42, Equation 1.

Hydrolysis of the monomers is avoided by adding alkaline stabilizers (for example 0.1 percent of triethanolamine) to the stored vinyl ethers. Stabilizers and impurities such as alcohol, acetaldehyde, and acetals are then removed before polymerization by washing with water or very dilute KOH. Vinyl ethers produce high molecular weight homopolymers when reacted in the presence of Lewis acid catalysts. The catalysts used are related to Zeigler catalysts, for example, diethyl aluminum chloride or Grignard reagents.

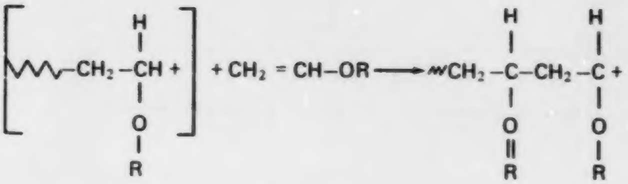
The propagation step proceeds as shown in Figure III-42, Equation 2, thereby producing a head-to-tail structure. The more highly branched the alkyl groups are, the greater the reactivity of monomer. Long chain alkyl ethers are generally less reactive than the short chain homologs. Aromatic vinyl ethers do not polymerize readily and are susceptible to side reactions such as rearrangements and condensations.

Vinyl ethers do not copolymerize readily with other vinyl ethers, but they readily form copolymers with a wide variety of ether monomers including dibutyl maleate, maleic anhydride, acrylonitrile, vinylidene chloride, vinyl chloride, vinyl acetate, and methyl acrylate.

Polyalkyl vinyl ethers are utilized primarily for their ability to serve as plasticizers for coatings, or because of their tackiness for use in adhesives. The methyl homopolymer is used as a plasticizer for coatings and is an aqueous adhesive tackifier. The vinyl methyl ether-maleic anhydride copolymer is used as a water thickening agent, suspending agent, and an adhesive.

Manufacture - Commercial processes are typical for the various polymerization techniques. Solution or bulk techniques are presently used in the U.S. Typical flow diagrams for these processes are shown in Figures III-43 and III-44. In the solution polymerization process, when a solvent-free product is desired, it is dried by heating

(1) $CH_2=CHOR + H_2O \xrightarrow{H+} [CH_2=CHOH] \xrightarrow{H+} CH_3CHO$

(2) 

$$\left[\sim CH_2-\underset{\underset{R}{|}}{\underset{O}{|}}{\overset{H}{\overset{|}{CH}}}\,^{+}\right] + CH_2=CH-OR \longrightarrow \sim CH_2-\underset{\underset{R}{\parallel}}{\underset{O}{|}}{\overset{H}{\overset{|}{C}}}-CH_2-\underset{\underset{R}{|}}{\underset{O}{|}}{\overset{H}{\overset{|}{C}}}\,^{+}$$

FIGURE III–42 TYPICAL REACTIONS TO FORM POLYVINYL ETHERS – INCLUDING MONOMER MANUFACTURE

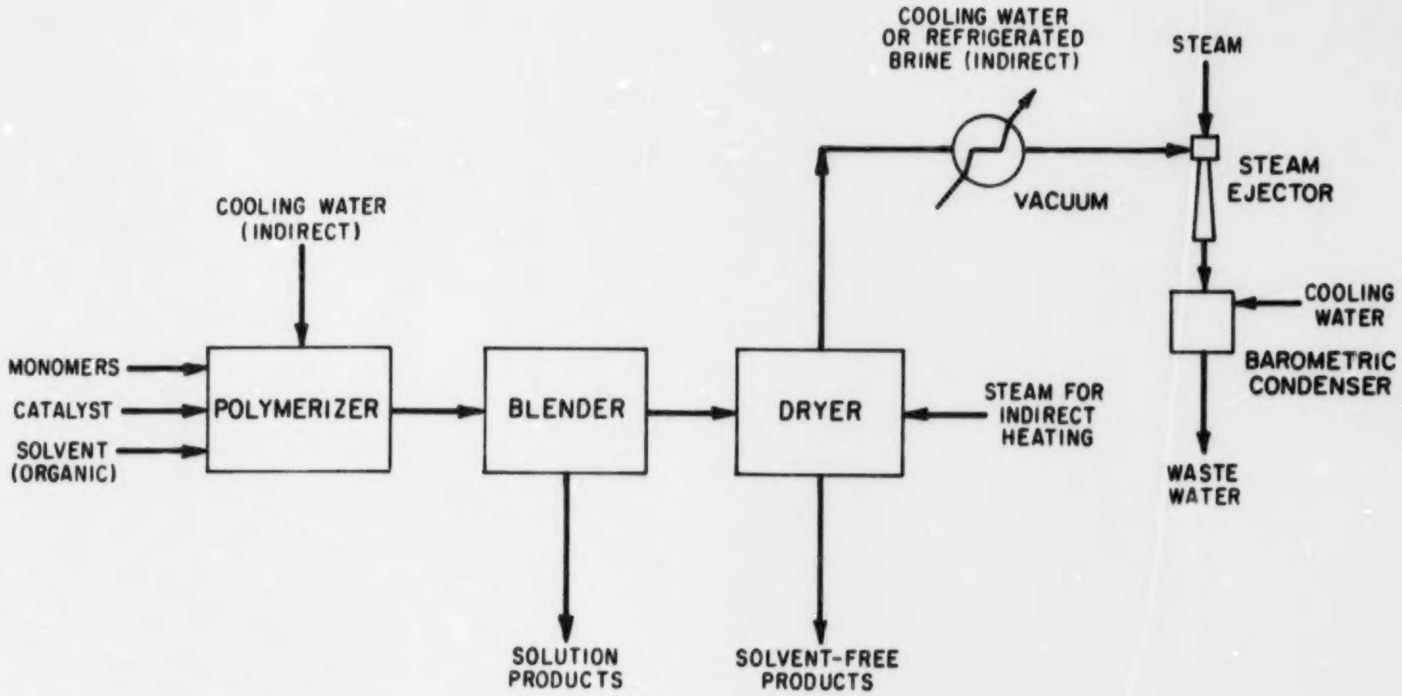

COOLING WATER OR REFRIGERATED BRINE (INDIRECT)
STEAM
STEAM EJECTOR
VACUUM
COOLING WATER (INDIRECT)
COOLING WATER
BAROMETRIC CONDENSER
MONOMERS
CATALYST
SOLVENT (ORGANIC)
POLYMERIZER
BLENDER
DRYER
STEAM FOR INDIRECT HEATING
WASTE WATER
SOLUTION PRODUCTS
SOLVENT-FREE PRODUCTS

FIGURE III-43 POLYVINYL ETHER PRODUCTION – SOLUTION POLYMERIZATION PROCESS

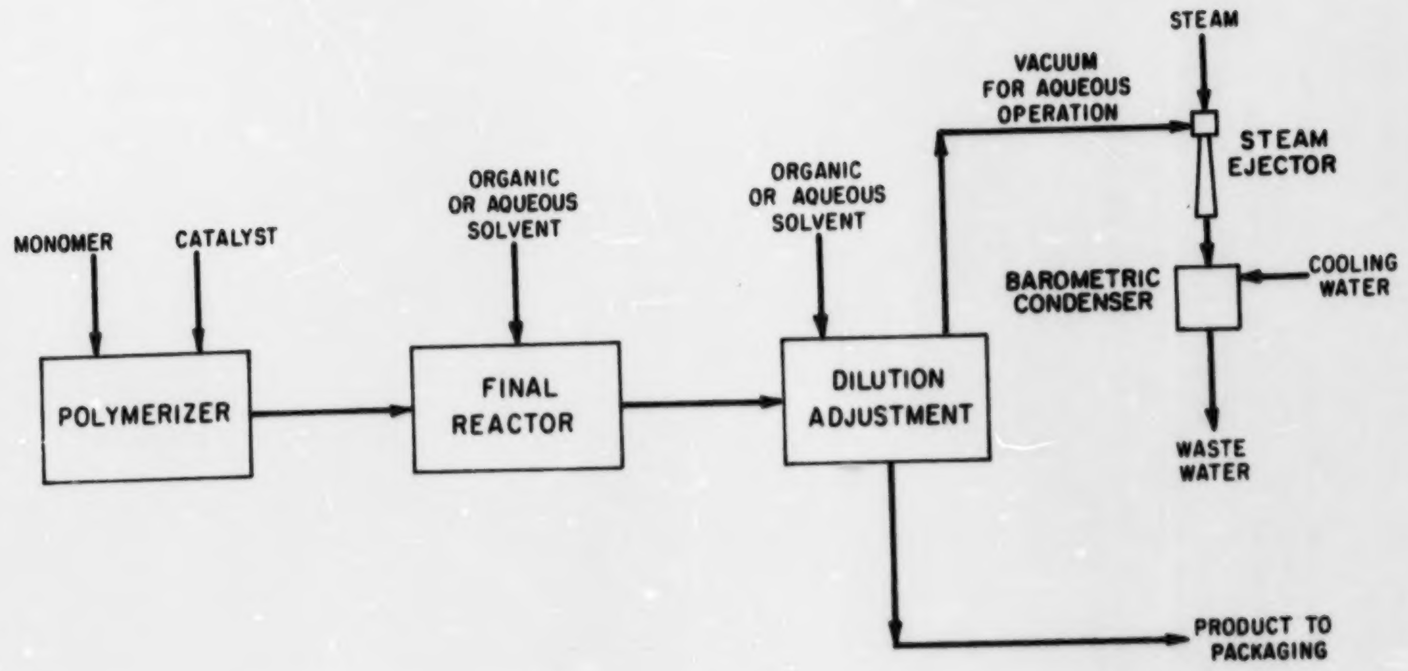

MONOMER
CATALYST
POLYMERIZER
ORGANIC OR AQUEOUS SOLVENT
FINAL REACTOR
ORGANIC OR AQUEOUS SOLVENT
DILUTION ADJUSTMENT
VACUUM FOR AQUEOUS OPERATION
STEAM
STEAM EJECTOR
BAROMETRIC CONDENSER
COOLING WATER
WASTE WATER
PRODUCT TO PACKAGING

FIGURE III-44 POLYVINYL ETHER PRODUCTION – BULK POLYMERIZATION PROCESS

under vacuum. In the bulk process, aqueous or organic solvent is sometimes added to the product depending on desired properties.

Waste Water Generation - Sources of waste water will depend upon the polymerization process employed. In solution polymerization, when no drying step is employed, there are no direct contact waste waters. When drying is employed, some contamination of the water from the steam ejector barometric condenser results.

There is no water of reaction in the polymerization of polyalkyl vinyl ethers (25).

Polyvinylidene Chlorides

Polyvinylidene chloride latex is commonly used for paper and film coatings. The latex is produced by emulsion polymerization of vinylidene chloride, frequently in the presence of another monomer. The equation in Figure III-45 expresses the reaction involved.

Manufacture - The polymerization is performed in water using an emulsifier, a peroxide, and a reducing agent such as sodium bisulfite. The reaction is conducted in an inert atmosphere, and after several hours it is complete.

Following the polymerization, the emulsion may be heated with steam to destroy components in the mixture that might generate odors on standing or in use, and is then ready for sale.

Waste Water Generation - Wastes developed in the process consist of tank washings. These wastes include a low level of all of the ingredients used, and suspended solids corresponding to the polymer produced (41).

$$n\left[CH_2 = CCl_2\right] \longrightarrow (CH_2{-}CCl_2)_n$$

FIGURE III–45 TYPICAL REACTION TO FORM POLYVINYLIDENE CHLORIDE

Polyvinyl Pyrrolidone

Polyvinyl pyrrolidone is a water soluble polymer characterized by unusual complexing and colloidal properties. It is available in pharmaceutical grades, a beverage grade, and in a grade suitable for textile leveling and stripping.

The monomer reactant is N-vinyl-2-pyrrolidone, shown in Figure III-46, Equation 1. This is a colorless liquid with a freezing point of 13.6°C (56.5°F), a boiling point of 96°C (204.8°F) at 50 mm, and 123°C (253.4°F) at 114 mm. It is completely miscible with water and most organic solvents. The monomer is manufactured by the vinylation of 2-pyrrolidone with acetylene in the presence of alkali metal salts of pyrrolidone.

The polymerization to the product polymer (shown in Figure III-46, Equation 2) is accomplished by ionic catalysis using boron trifluoride or potassium amide. The polymerization may also be catalyzed with free radical catalysts such as hydrogen peroxide, benzoyl peroxide, or azobisisobutyronitrile. Also, highly purified vinyl pyrrolidone combines with atmospheric oxygen to give peroxide-type compounds which themselves act as polymerization catalysts. Since the vinyl amides are hydrolyzed under acidic conditions, polymerizations are best carried out at neutral or basic pH in water. The polymerization reaction is as shown in Equation 3 of Figure III-46.

A typical batch solution process for homopolymerization which was applied on a semi-industrial scale is as follows. One-half of a 30 percent solution of purified vinyl pyrrolidone in water was added to the reaction vessel. The remainder was added slowly during the reaction. Catalysis was accomplished by addition of 0.2 percent hydrogen peroxide and 0.1 percent ammonia. The reaction was complete in 2 to 3 hours. It was found that molecular weight increases with ammonia concentration and is directly proportional to monomer concentration up to about 30 percent. Above 30 percent, molecular weight was found to be inversely proportional to catalyst concentration.

Copolymerization of N-vinyl-2-pyrrolidone has been successfully accomplished with a number of co-monomers. Among these are ethylene glycol monovinyl ether, ethylene, laurylacrylamide, C_{12} to C_{18} methacrylate, divinyl carbonate, cinnamic acid, and crotonaldehyde. A typical process utilizes solvents such as alcohol or benzene, a

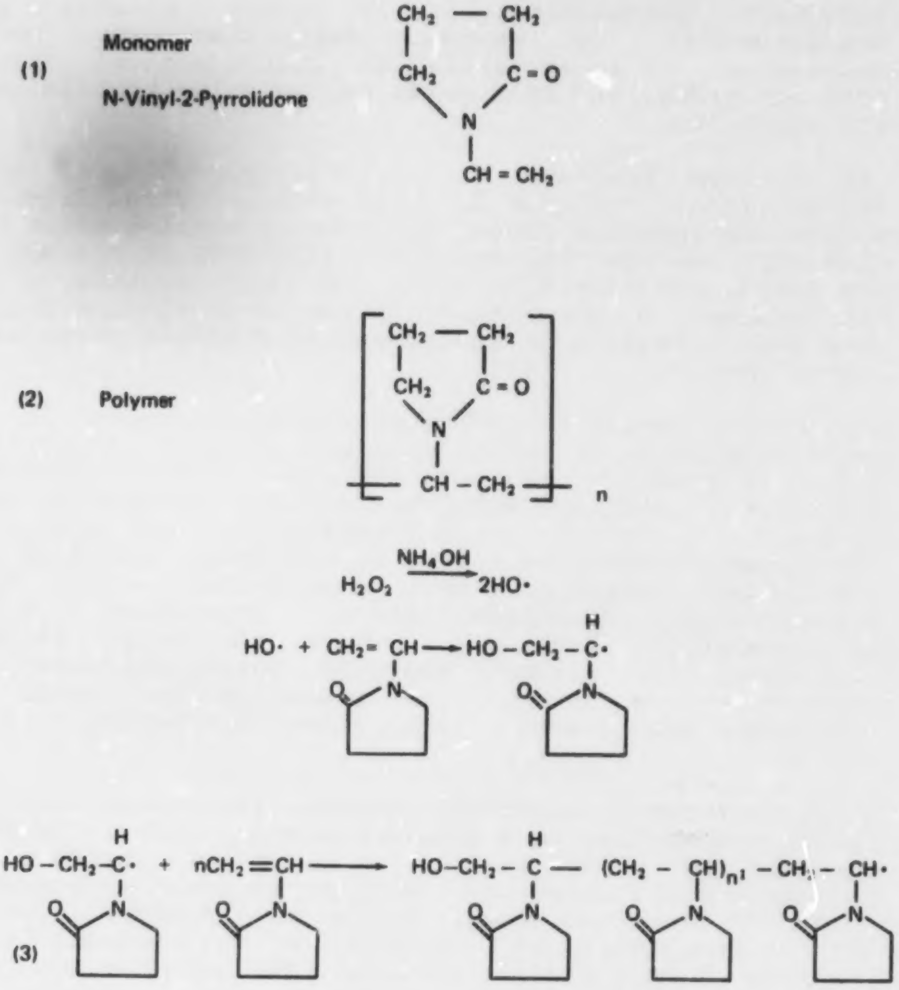

(1)
Monomer
N-Vinyl-2-Pyrrolidone
(2)
Polymer
n
NH₄OH
H₂O₂
2HO·
HO· + CH₂= CH → HO – CH₂ – C·
(3)
HO – CH₂–C· + nCH₂ ═CH → HO–CH₂ – C — (CH₂ – CH)n¹ – CH₂ – CH·

FIGURE III–46 TYPICAL REACTIONS TO FORM POLYVINYL PYRROLIDONE

reaction temperature of 50-75°C (122-167°F), and catalyst at concentrations 0.1 to 1 percent. Typical catalysts are benzoyl peroxide, lauroyl peroxide, and azobisisobutyronitrile.

Graft polymerization has also been readily accomplished in a number of cases.

The homopolymer polyvinyl pyrrolidones are produced in four viscosity grades corresponding to average number molecular weights: 10,000, 40,000, 160,000, and 360,000. Pharmaceutical grades, beverage grades, and textile leveling and stripping grades are produced domestically. Copolymers with vinyl acetate of varying proportions are also marketed domestically.

Manufacture - Polyvinyl pyrrolidone is produced on commercial scale by polymerization in water at 20-60 percent concentration, depending upon the desired product viscosity. Reaction is carried out with catalysis by hydrogen peroxide and ammonia in the temperature range 50-80°C (122-176°F). The product is spray dried. An alternative commercial process is polymerization in water using azobisisobutyronitrile at 50-60°C (122-140°F).

Waste Water Generation - The typical solution polymerization in water would yield only a small waste water stream since the solvent is recycled whenever possible. The polymer product is probably washed, depending upon its end use, and the wash water would contain small fractions of all agents in the reaction mix including some catalyst. There is no water of reaction (25).

Silicones

Manufacture - Plants producing silicones typically produce a wide variety of chemicals incorporating silicone. Silicone chemistry is complex, and the discussion here is limited to indicating the processes conducted and the types and scope of wastes generated. Figures III-47 and III-48 are simplified flowsheets which suggest the complexity of silicones plants. Figure III-47 shows processes used for production of several different chlorosilanes and hydrolysis of dimethyl dichlorosilane to dimethyl silicone fluid. Figure III-48 shows transformation of the dimethyl silicone fluid to finished fluids, greases, emulsions, rubber, and resins. These figures do not include several processes conducted at the plants.

All of the plants we have examined purchase silicon metal and react it with a wide range of chemicals, used in several steps. The following processes may be conducted at a silicone plant:

1. Production of methyl chloride, generally by reaction of methanol and hydrogen chloride, Figure III-49, Equation 1.

   Methyl chloride is used in production of methylated chlorosilanes. Other organic chlorides, alkyl or aryl, are used also; e.g., phenyl chloride.

   Methyl chloride may be purchased by a silicones plant rather than being manufactured there. As far as we are aware, other organic halides are always purchased.

2. Chlorosilane production. For the methyl fluids, methyl chlorosilanes are produced by the reaction shown in Figure III-49, Equation 2.

Other organic chlorides (see above) would be used to generate other chlorosilanes. The mixture of products produced in the direct process are separated by fractional distillation to provide each component; dimethyldichlorosilane must be very pure for use in subsequent syntheses (see below). Some of the chlorosilanes (probably methyl trichlorosilane) have limited use, and are wasted.

The above equation represents the "direct" process for making chlorosilanes; it is widely used for the methyl compounds, the phenyl compounds, and perhaps others.

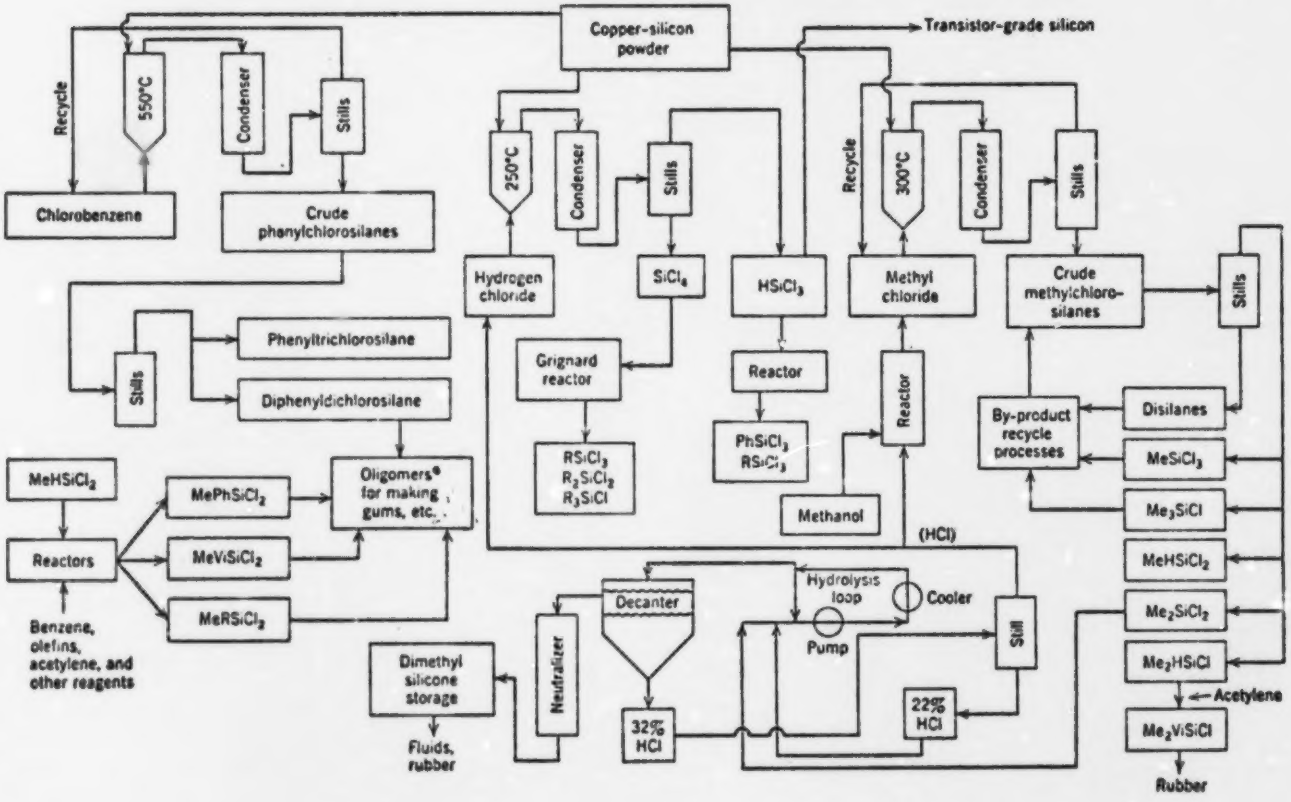

Copper-silicon powder
Transistor-grade silicon
Recycle
550°C
Condenser
Stills
Chlorobenzene
Crude phenylchlorosilanes
Stills
Phenyltrichlorosilane
Diphenyldichlorosilane
250°C
Condenser
Stills
Hydrogen chloride
SiCl$_4$
Grignard reactor
RSiCl$_3$
R$_2$SiCl$_2$
R$_3$SiCl
HSiCl$_3$
Reactor
PhSiCl$_3$
RSiCl$_3$
Recycle
300°C
Condenser
Stills
Methyl chloride
Reactor
Methanol
(HCl)
Crude methylchlorosilanes
Stills
By-product recycle processes
Disilanes
MeSiCl$_3$
Me$_3$SiCl
MeHSiCl$_2$
Me$_2$SiCl$_2$
Me$_2$HSiCl
Acetylene
Me$_2$ViSiCl
Rubber
MeHSiCl$_2$
Reactors
Benzene, olefins, acetylene, and other reagents
MePhSiCl$_2$
MeViSiCl$_2$
MeRSiCl$_2$
Oligomers* for making gums, etc.
Hydrolysis loop
Cooler
Pump
Still
Decanter
32% HCl
22% HCl
Neutralizer
Dimethyl silicone storage
Fluids, rubber

FIGURE III-47 PRODUCTION OF SILANE MONOMERS, OLIGOMERS AND DIMETHYL SILICONE FLUID

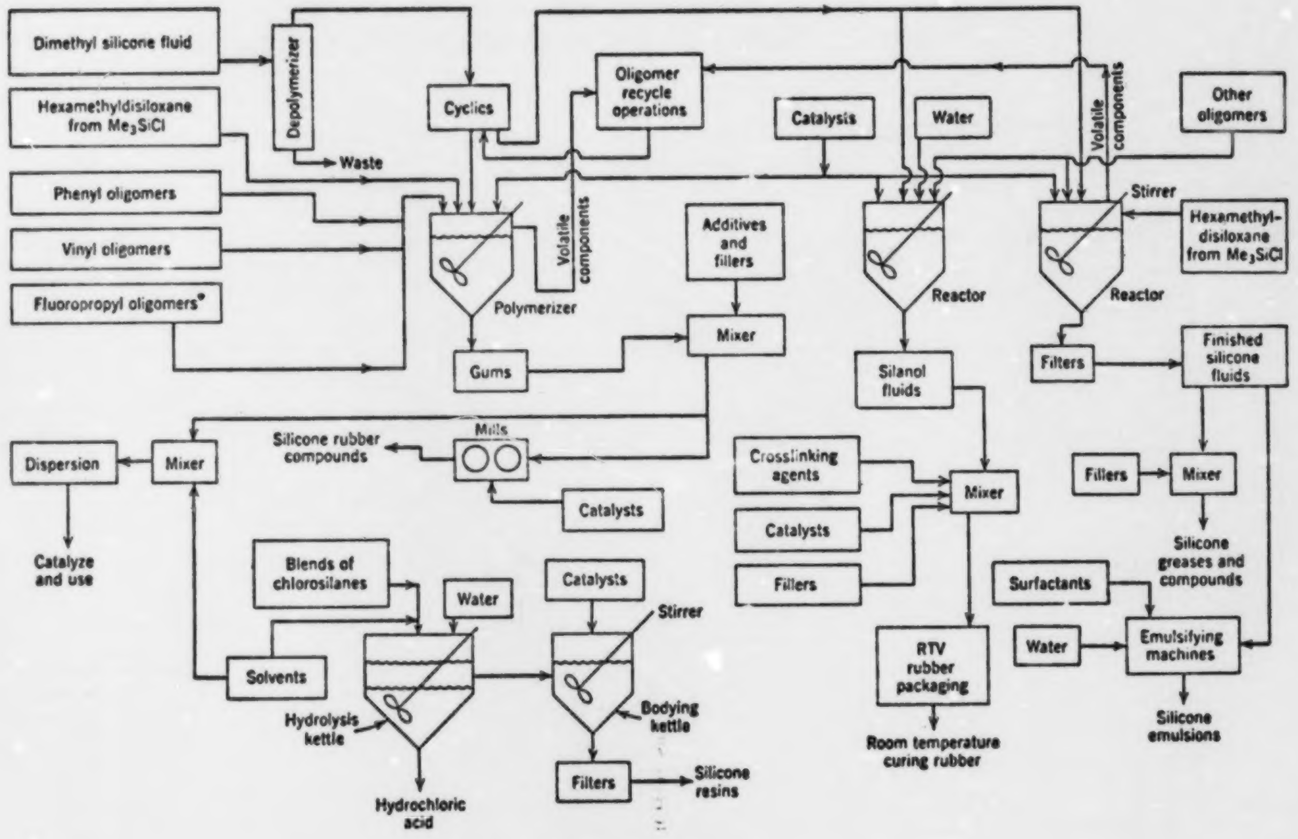
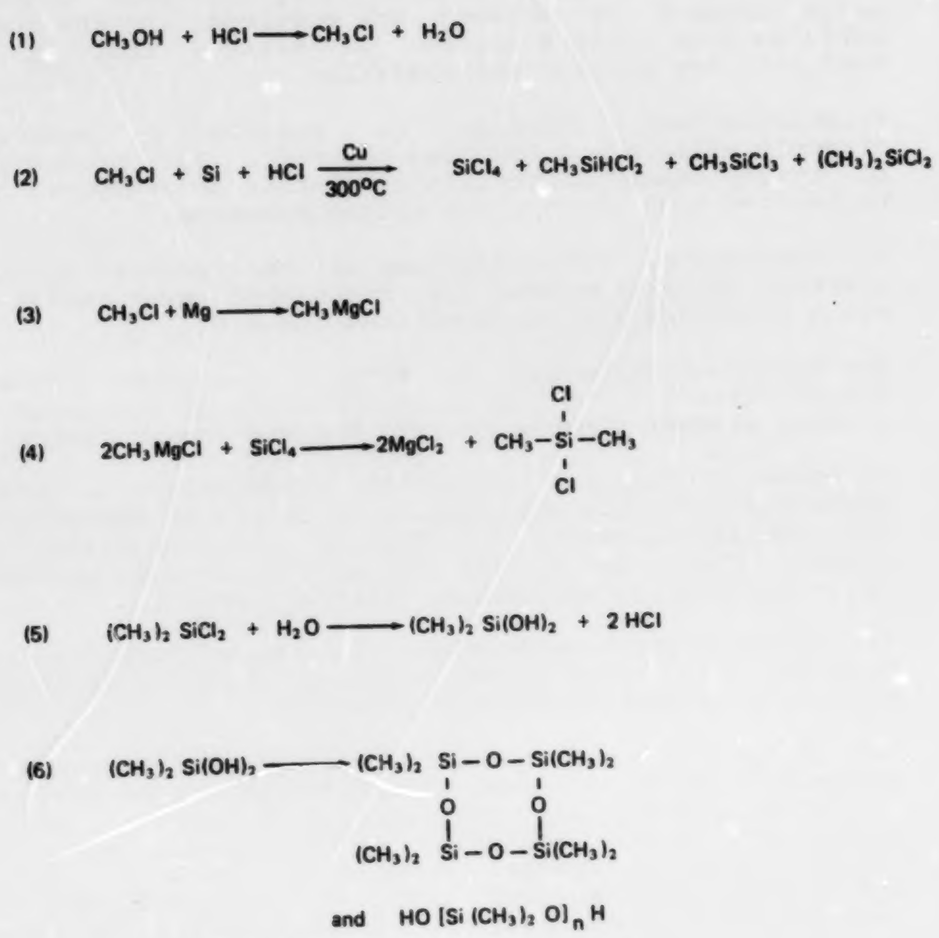

Dimethyl silicone fluid
Hexamethyldisiloxane from Me$_3$SiCl
Phenyl oligomers
Vinyl oligomers
Fluoropropyl oligomers*
Depolymerizer
Waste
Cyclics
Oligomer recycle operations
Volatile components
Polymerizer
Gums
Additives and fillers
Mixer
Catalysis
Water
Reactor
Volatile components
Other oligomers
Stirrer
Hexamethyl-disiloxane from Me$_3$SiCl
Reactor
Filters
Finished silicone fluids
Silanol fluids
Crosslinking agents
Catalysts
Fillers
Mixer
RTV rubber packaging
Room temperature curing rubber
Fillers
Mixer
Silicone greases and compounds
Surfactants
Water
Emulsifying machines
Silicone emulsions
Mills
Silicone rubber compounds
Catalysts
Dispersion
Mixer
Catalyze and use
Blends of chlorosilanes
Water
Solvents
Hydrolysis kettle
Hydrochloric acid
Catalysts
Stirrer
Bodying kettle
Filters
Silicone resins

FIGURE III-48 PRODUCTION OF SILICONE FLUIDS, GREASES, COMPOUNDS, EMULSIONS, RESINS AND RUBBER



(1) $CH_3OH + HCl \longrightarrow CH_3Cl + H_2O$

(2) $CH_3Cl + Si + HCl \xrightarrow[300^{o}C]{Cu} SiCl_4 + CH_3SiHCl_2 + CH_3SiCl_3 + (CH_3)_2SiCl_2$

(3) $CH_3Cl + Mg \longrightarrow CH_3MgCl$

(4) $2CH_3MgCl + SiCl_4 \longrightarrow 2MgCl_2 + CH_3-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{Si}}-CH_3$

(5) $(CH_3)_2SiCl_2 + H_2O \longrightarrow (CH_3)_2Si(OH)_2 + 2HCl$

(6)
$$(CH_3)_2Si(OH)_2 \longrightarrow \begin{array}{rccl} (CH_3)_2 & Si & -O- & Si(CH_3)_2 \\ & | & & | \\ & O & & O \\ & | & & | \\ (CH_3)_2 & Si & -O- & Si(CH_3)_2 \end{array}$$

and $HO[Si(CH_3)_2O]_nH$

FIGURE III–49 TYPICAL REACTIONS TO FORM SILICONES

Chlorosilanes may also be made by a Grignard process, represented by Equations 3 and 4 in Figure III-49. The Grignard process finds limited use, in part because large amounts of solvent are required, and the metal salts go into a waste stream. We believe that it is used only for special chlorosilanes.

Trichlorosilane ($HSiCl_3$) is produced by reacting directly silicon and hydrogen chloride. For production of still other chlorosilanes, olefins or acetylene may be reacted with appropriate silane monomers.

3. Hydrolysis. For production of the methyl fluids, dimethyl dichlorosilane is hydrolyzed with water as shown in Figure III-49, Equations 5 and 6.

The cyclic siloxane may be further processed to the linear polymer. The linear products are manufactured in a broad viscosity range to give the well-known fluids.

Silicone fluids are often sold as emulsions in water; production of these mixtures involves use of emulsifiers and special equipment. In addition, the viscosity of certain fluids may be substantially increased, probably by cross-linking, to provide silicone greases.

4. Silicone resin production. The resin products are branched and cross-linked siloxane polymers, generally sold as solutions in organic solvents.

The resins are manufactured by hydrolysis of mixtures of chlorosilanes in solvents. The mixtures may be complex, including mono-, di- and trichloro-silanes having different organic radicals, alkoxysilanes, and other silanes bearing special functional groups. After hydrolysis, the aqueous layer is separated and the organic phase is neutralized. A catalyst may be added to the organic solution, and the mixture may be heated to polymerize the dissolved chemicals.

5. Elastomer production. Silicone elastomers are produced from high molecular weight fluids, fillers, and curing agents. The mixtures are often called compounds.

Two types of polymer-filler mixtures are produced, those which cure to rubber by application of heat and those which are cured at room temperature. Catalysts used for products cured at room temperature may be tin or organotin salts.

6. Specialties production. For our purposes, specialties constitute materials which are produced in significant amounts at a single silicones plant but in minor amounts, if at all, at others. We have included surfactants, coupling agents and fluorosilicones as specialties, but other products may also be classified in this group. It is characteristic of silicones plants that new products are constantly being developed and offered commercially.

Surfactants are produced by reaction of silicone fluids with polyethylene oxide, or polyethylene oxide-polypropylene oxide. The products are water soluble.

Coupling agents are monomeric silanes which serve as glass surface primers to increase the adhering strength of a resin subsequently applied. The typical final composition is glass-silane-resin. The resin may be epoxy, polyester, melamine, or other. One coupling agent which has been used is aminopropyl triethoxy silane. Production of such chemicals generally involves reaction of a chlorosilane with an appropriate organic compound, followed by exchange of the halogen atoms with alcohol groups. Coupling agents are produced in significant quantities at one manufacturing location. These resins require a vacuum to be applied to the batch reactor kettle during the hydrolysis reaction (5) in Figure 49. Existing plants employ once-through barometric condensers to achieve the vacuum; use of such condensers increases the process water flow from the vicinity of 17,000 to 27,000 gallons per 1000 pounds of product. These extra waters cannot be recycled until concentrated, as is practiced in the manufacture of polyesters and alkyds, for instance, since the materials of construction of the process equipment will not withstand the more concentrated hydrochloric acid. New plants, however, could incorporate such a change without undue penalty. On existing plants, this additional condenser water may be used as scrubber water for incineration, thereby not adding to the total hydraulic load by the addition of incineration. Surface condensers of current design are very expensive for this application due to the need for hastalloy type alloys for the metal parts in contact with the process waters, and are also subject to frequent plugging from the products of reaction.

Waste Water Generation - Resin production generates significant amounts of acid wastes due to the liberation of hydrogen chloride in the hydrolysis step. The acid may be recycled, for example in the production of methyl chloride, but in many cases it is impractical to recover it. Organic solvent wastes, such as naphtha or toluene, are also produced. Most of the solvents are recovered, but trace quantities may appear in the waste water. Quantitative information on the waste water generated in silicone polymerization processes is not documented in the literature (25, 41).

Source of heavy metals - copper catalyst used for the chlorosilane production process enters the waste water during the hydrolysis step and in subsequent water of reaction produced during polymerization. Fluorides may be present in the waste water where fluorosilicones are being manufactured.

Spandex Fibers

Spandex fibers are made from conventional polyurethane ingredients. Textile Organon (43) defines spandex fibers as being composed of "at least 85 percent by weight of a segmented polyurethane." In common with other fiber processing reactions, extremely careful control must be maintained in raw materials specifications and reaction techniques to insure adequate quality of fiber.

The rubber-like qualities of the spandex fibers result from the formation of a polyurethane composed of alternating sections of soft and hard segments. The hard segments are considered to be rigid and impart elasticity by limiting the viscous flow which results from the soft segments. The soft segments are long-chained molecules terminated with hydroxyl groups. Common examples are polyadipate which is the reaction product of adipic acid and a glycol (Figure III-50, Equation 1), polytetramethylene glycol (Equation 2), and polycaprolactone (Equation 3). These soft segments are then reacted with a diisocyanate, most generally toluene diisocyanate (TDI) (Equation 4), or methylene bis(4-phenol isocyanate) (MDI) (Equation 5), to give an isocyanate-terminated prepolymer containing urethane linkages. The structure of a typical MDI-terminated polyadipate prepolymer is shown in Figure III-50, Equation 6. This prepolymer is then reacted with either a diamine (such as ethylene diamine) or hydrazine to form the final spandex fiber; the reaction is shown in Figure III-50, Equation 7. Various additives such as delusterants (titanium dioxide), ultraviolet absorbers, and antioxidants are also added to obtain various properties.

Manufacture - Spandex fiber can be produced by wet or dry solution spinning processes, reaction spinning, or melt spinning.

One major U.S. fiber producer, uses the dry spinning process. In this the heated polymer, dissolved in a solvent such as dimethyl formamide, is extruded through a spinnerette into a column of circulating hot air which serves to evaporate the solvent and thereby solidify the filaments. A schematic diagram of the dry spinning process is shown in Figure III-51.

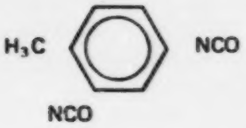
Another U.S. producer produces spandex fibers by the wet spinning process. This process is similar to that employed by DuPont in that a spinning solution is used, but instead of spinning into a column of circulating hot air, the spinning solution is spun into a water bath which serves to

(1) $H(OROCO\,CH_2\,CH_2\,CH_2\,CH_2\,CO)_nOROH$

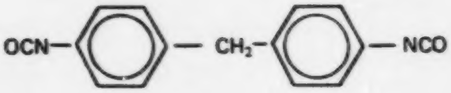
(2) $H\,[O(CH_2)_3CH]_nOH$

(3) $H\,[O\,(CH_2)_5\,CO]_n\,OROH$

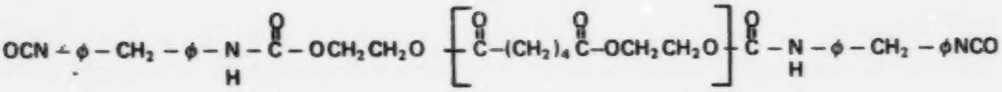
(4)



(5)

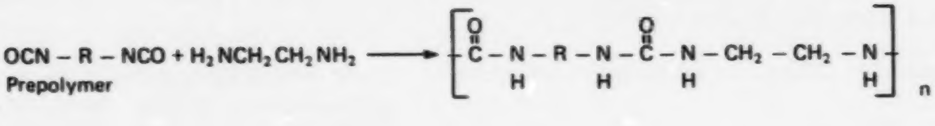


(6)



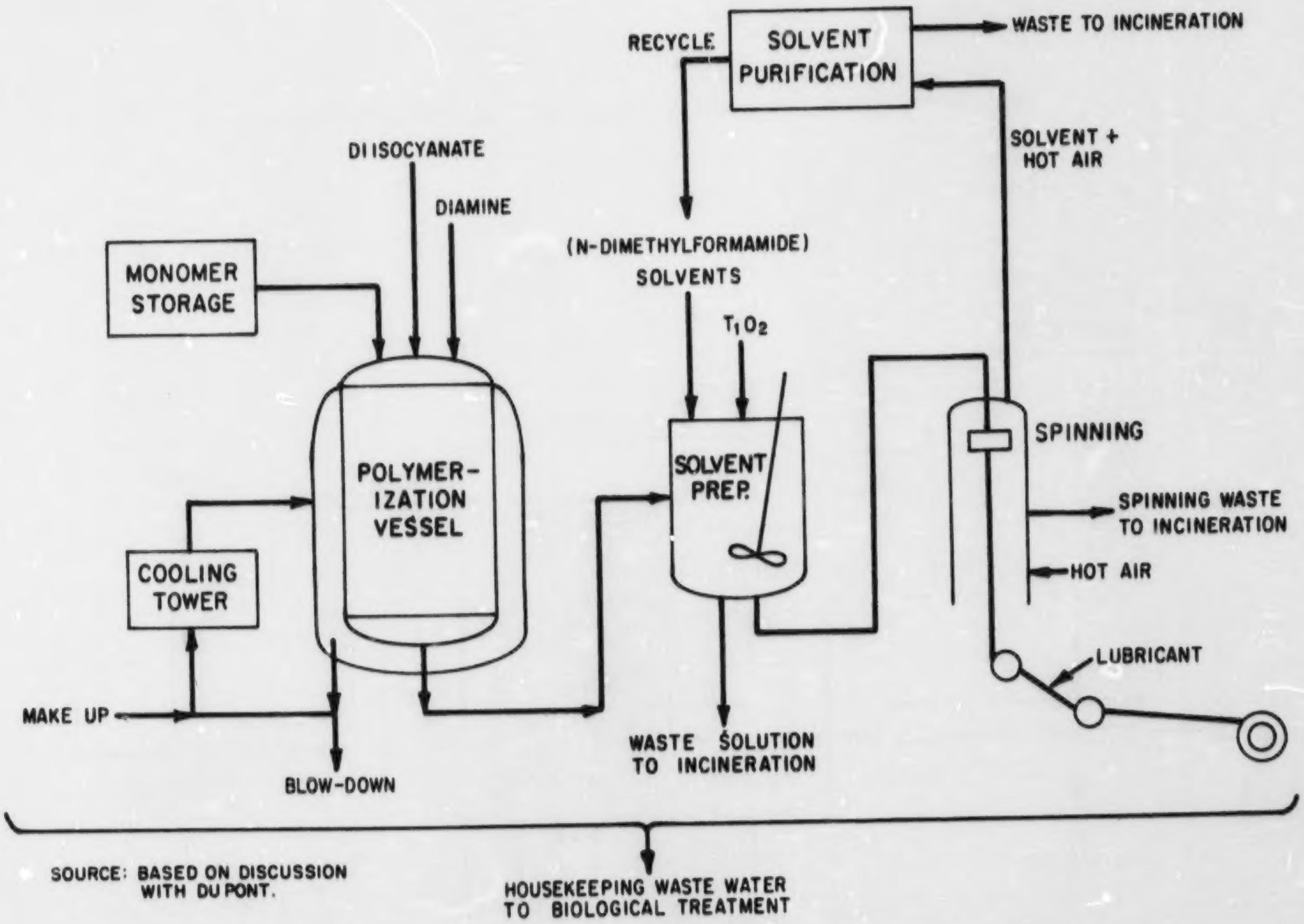
$$OCN-\phi-CH_2-\phi-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-OCH_2CH_2O\left[\overset{O}{\overset{\|}{C}}-(CH_2)_4\overset{O}{\overset{\|}{C}}-OCH_2CH_2O\right]\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\phi-CH_2-\phi NCO$$

(7)



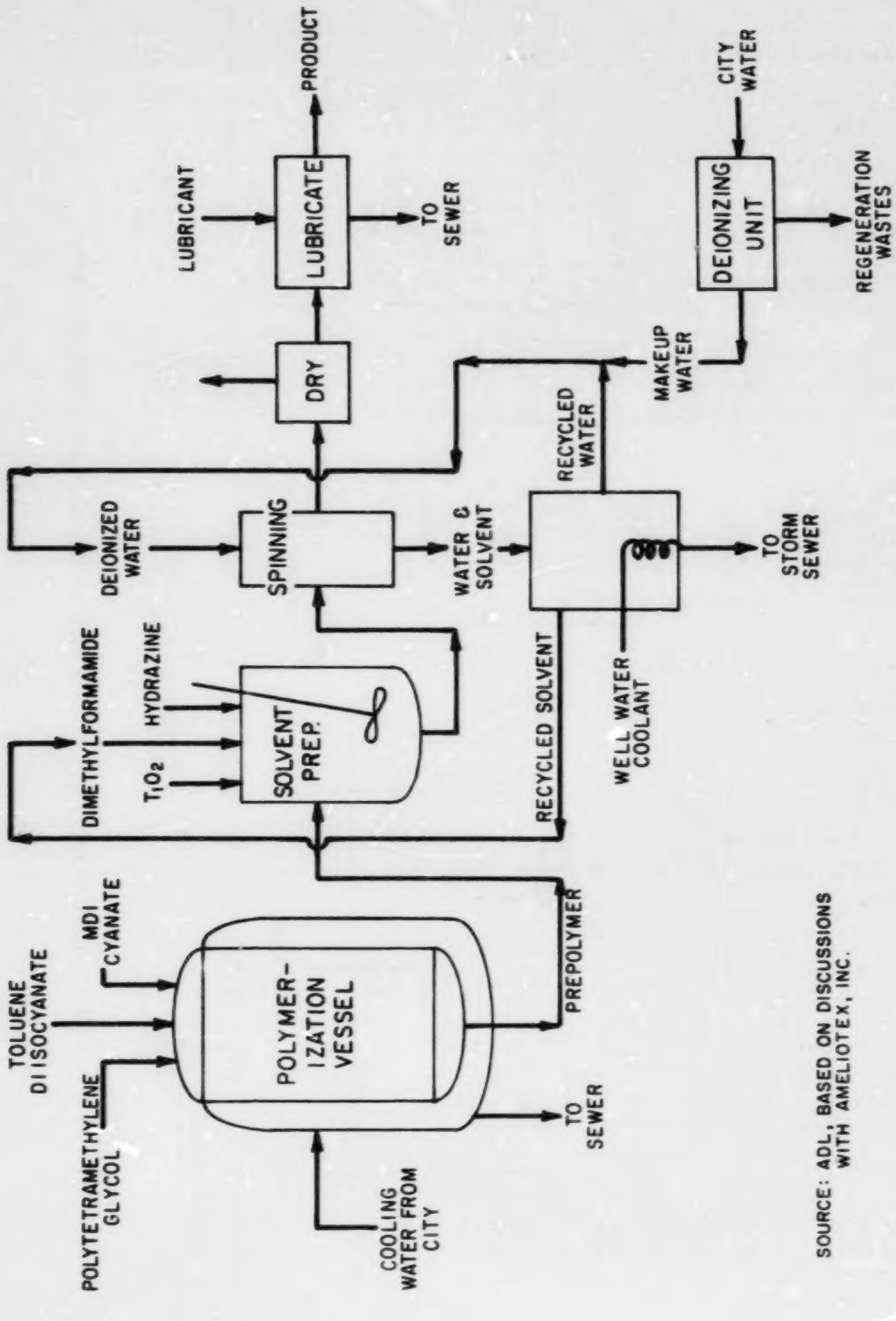
$$\underset{\text{Prepolymer}}{OCN-R-NCO}+H_2NCH_2CH_2NH_2\longrightarrow\left[\overset{O}{\overset{\|}{C}}-\underset{H}{N}-R-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-CH_2-CH_2-\underset{H}{N}\right]_n$$

FIGURE III–50 TYPICAL REACTIONS TO FORM SPANDEX FIBERS


RECYCLE
SOLVENT PURIFICATION
WASTE TO INCINERATION
SOLVENT + HOT AIR
DIISOCYANATE
DIAMINE
(N-DIMETHYLFORMAMIDE)
SOLVENTS
MONOMER STORAGE
T_1O_2
POLYMER-IZATION VESSEL
SOLVENT PREP.
SPINNING
SPINNING WASTE TO INCINERATION
HOT AIR
COOLING TOWER
LUBRICANT
MAKE UP
BLOW-DOWN
WASTE SOLUTION TO INCINERATION
HOUSEKEEPING WASTE WATER TO BIOLOGICAL TREATMENT

SOURCE: BASED ON DISCUSSION WITH DU PONT.

FIGURE III-51 SPANDEX FIBER PRODUCTION – DRY SPINNING PROCESS


POLYTETRAMETHYLENE GLYCOL
TOLUENE DIISOCYANATE
MDI CYANATE
POLYMER-IZATION VESSEL
COOLING WATER FROM CITY
TO SEWER
PREPOLYMER
DIMETHYLFORMAMIDE
T_iO_2
HYDRAZINE
SOLVENT PREP.
RECYCLED SOLVENT
WELL WATER COOLANT
DEIONIZED WATER
SPINNING
WATER & SOLVENT
TO STORM SEWER
RECYCLED WATER
MAKEUP WATER
DRY
LUBRICANT
LUBRICATE
TO SEWER
PRODUCT
CITY WATER
DEIONIZING UNIT
REGENERATION WASTES

SOURCE: ADL, BASED ON DISCUSSIONS WITH AMELIOTEX, INC.

FIGURE III-52 SPANDEX FIBER PRODUCTION – WET SPINNING PROCESS

extract the solvent and coalesce a multifilament yarn. A schematic of the process based on a discussion with Ameliotex is shown in Figure III-52.

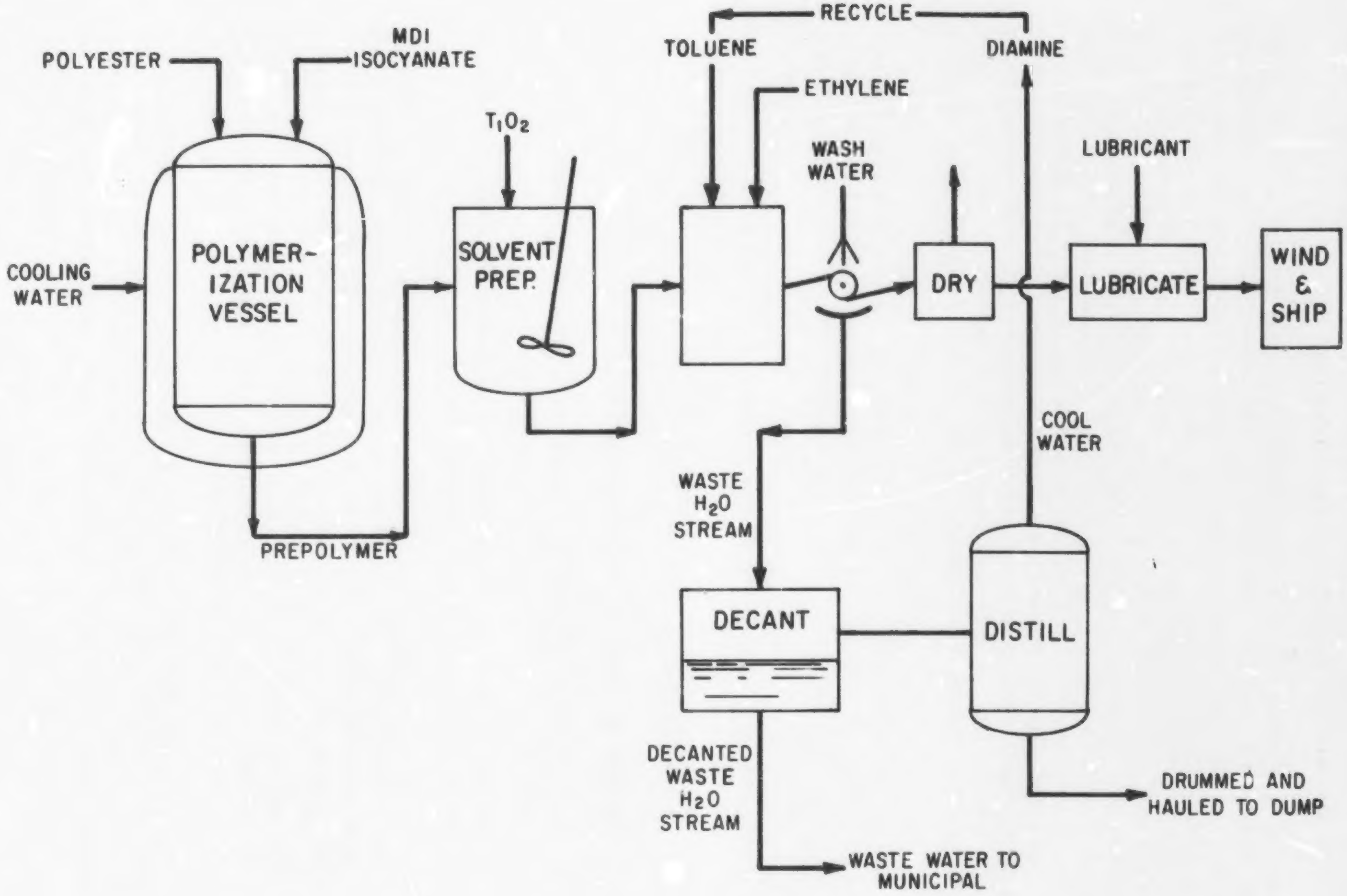
Another U.S. producer produces spandex fibers by a variation of wet spinning which is known as reaction or chemical spinning. The isocyanate-terminated prepolymer is extruded into a bath containing toluene and a diamine (ethylene diamine). The diamine reacts with the prepolymer by crosslinking or chain extending to convert it to a solid elastomeric fiber. Although individual filaments are produced in this way, usually the individual fibers are brought together to form a coalesced, multifilament yarn. After leaving the ethylene diamine/toluene spin bath, the coalesced yarn is washed with water, dried, and lubricated prior to winding. A schematic of the process based on discussions and communications with Globe is shown in Figure III-53.

Waste Water Generation - In addition to cooling water discharge, the producer which uses the dry spinning process, reports the following sources of wastes and corresponding handling methods:

1. Waste polymer -- incinerated.
2. Waste solution from the solution preparation step -- incinerated.
3. Spinning waste -- incinerated.
4. Normal housekeeping water and equipment washout -- biological treatment.
5. Waste from the solvent purification and recycle step -- biological treatment.

In the wet spinning process there are cooling water discharges, regeneration wastes from the water deionizing unit, and occasional wastes resulting from cleanout of lubricant (spin finish) tanks. Note that the solvent water mixture from the spinning bath is transferred to a recovery unit from which both solvent and water are recycled to the spinning bath. The company states that the only water loss is by evaporation to the atmosphere.

The primary source of waste from the other producers' reaction or chemical spinning process originates from the washing step which follows the spinning bath. This stream containing wash water, toluene, and ethylene diamine is



POLYESTER
MDI ISOCYANATE
COOLING WATER
POLYMER-IZATION VESSEL
PREPOLYMER
T_1O_2
SOLVENT PREP.
TOLUENE
RECYCLE
DIAMINE
ETHYLENE
WASH WATER
DRY
LUBRICANT
LUBRICATE
WIND & SHIP
COOL WATER
WASTE H_2O STREAM
DECANT
DISTILL
DECANTED WASTE H_2O STREAM
WASTE WATER TO MUNICIPAL
DRUMMED AND HAULED TO DUMP

FIGURE III-53 SPANDEX FIBER PRODUCTION – REACTION SPINNING PROCESS

passed to a continuous decanter which allows separation of toluene and water by gravity. Toluene is removed and purified by distillation prior to being recycled to the spin bath. Solid dregs remaining after distillation are drummed and hauled to a landfill. In the method used by Globe, the continuous decanter has a retention time of 160 minutes. This is said to be sufficient to give a water effluent (containing a faint odor of toluene) which is subsequently discharged to a municipal sewage system (41, 43).

Other Pollutants

Depending on the particular waste water chemical conditions and the analytical methods used, cyanides may be detected due to the presence of isocyanates. Oil and grease presence is due to lubricants used in the spandex fiber after extrusion. Organic nitrogen derives from the presence of ethylene diamine.

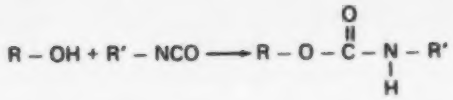
Urethane Prepolymers

The reaction of a compound containing a hydroxyl (-OH) group with a compound containing an isocyanate (-NCO) group produces a urethane linkage as indicated in Figure III-54, Equation 1.

Polyurethane resins are produced by the reaction of polyols (which are compounds containing two or more hydroxyl groups) with polyisocyanates (which are compounds containing two or more isocyanate groups) to form a polymer network with many urethane linkages. In the polyurethane there may also be other types of chemical linkages. For instance, if water is present in the reaction mixture either as a result of intentional addition of a minor amount of water or accidental presence as humidity, the -NCO group can react with a water molecule to produce an amine plus carbon dioxide (Figure III-54, Equation 2). Another isocyanate group can then react with the amine to produce a biuret linkage. Additional -NCO groups can also react with a hydrogen of the urethane linkage (Equation 1, Figure III-54) to produce an allophanate linkage. However, as long as the primary linkages in the polymer network are urethane, the product is known as a polyurethane. There is a wide range (literally hundreds) of polyols and several polyisocyanates that can be utilized to make polyurethanes with a wide range of properties.

In some cases, prepolymers are utilized to make the polyurethane resin. A prepolymer in the common commercial form is a liquid reaction product of a polyol with an excess of isocyanate to produce a low molecular weight polymer containing reactive isocyanate end groups as exemplified by Equation 3 in Figure III-54. This low molecular weight polymer normally becomes one part of a two-component system in which the second component is additional polyol with which the prepolymer can react to form a cross-linked cured urethane.

There are a number of reasons for using the prepolymer technique rather than the one-shot approach in which the isocyanate, polyol, and other components of a formulation are simply mixed together and allowed to react. The prepolymer approach often provides better control of rate of reaction and improved compatibility and mixing characteristics in the components. Improved product properties can often be obtained both through better control of the reaction and through the use of different polyols in making the prepolymer and for the final curing. Another important reason for using the prepolymer technique in polyurethanes

(1) 

$$R-OH+R'-NCO \longrightarrow R-O-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-R'$$

(2) $R'-NCO + H_2O \longrightarrow R'-NH_2 + CO_2$

(3) $3R(NCO)_2 + HO\,R'-OH \longrightarrow$

$OCN-R(NHCOO-R'-OCO\,NHR)_2\,NCO$

FIGURE III–54 TYPICAL REACTIONS TO FORM URETHANE PREPOLYMERS

which utilize relatively low molecular weight polyisocyanates such as toleuene diisocyanate (TDI) is that prereaction of the polyol with the isocyanate reduces the isocyanate vapor pressure and therefore lowers the toxicity of the formulation.

Most large volume polyurethane products such as flexible and rigid foams are produced primarily by the one-shot technique in which all components are blended together with no prereaction. The one-shot approach is used for large volume products because it is the most economical method to make polyurethanes. Prepolymers are generally used where smaller volumes and more specialized applications of polyurethanes are involved. For instance, foam systems that are sold as two-component liquid formulations for field spraying or cast-in-place applications frequently utilize prepolymers. Similarly, for other high value products where maximum control of the reaction is necessary, prepolymers are frequently used. Such applications include cast elastomers, sealants, adhesives, and two-component and air cure polyurethane coatings.

Manufacture - Prepolymers are commonly made by batch procedures although continuous processing techniques have been developed. In batch processing, a reactor jacketed for steam heating and water cooling is the only basic equipment required. Auxiliary equipment includes a feed system to place materials in the reactor and, frequently, a holding tank to which two or more batches of prepolymer can be transferred from the reactor and blended as necessary prior to transfer to a shipping container. The prepolymerization reaction is a simple addition reaction with no water or by-products produced. Throughout the process, the raw materials and the prepolymer must be stored or processed under a blanket of dry nitrogen or other inert gas because the isocyanate will react rapidly with any moisture present and will thus be converted to an amine and deactivated.

The continuous processes involve primarily the use of scraped film heat exchangers as the primary processing equipment but are analogous to the batch operation in other ways including maintenance of a nitrogen blanket over the raw materials and the prepolymer to eliminate any exposure to atmospheric moisture.

Waste Water Generation - Basically there is no water involved in the prepolymer production except for minor amounts which may purposely be added to the mix to produce some biuret linkages. In fact, every effort is made to assure that all unwanted water is excluded both from the feed materials and the product because the isocyanate will rapidly react with any water to form an unwanted amine. Even a minor amount of such unplanned reaction drastically changes the properties of the prepolymer and may even cause it to gel in the reactor or drum. The only water used is in the cooling jacket of the reactor, and this is completely separated from the reaction mixture. It is unlikely that any water would be used for cleaning a reactor between batches because the water would produce a rapid cure of the prepolymer and make the cleaning operation more difficult. In addition, the reactor would have to be thoroughly dried before processing of a new batch could begin. There is a remote possibility that in some instances a water miscible solvent might be used to clean the reactor and the solvent-prepolymer solution then mixed with water in order to react with the prepolymer, and that such contaminated water might be discharged. We are not aware of any such operations, and the possibility of such contamination occurring on any significant scale is remote because of the significant loss of raw materials that would be involved (25).

SECTION IV

INDUSTRY CATEGORIZATION

The most effective means of categorizing the resin segment of the synthetics and plastics industry was to determine if the two most relevant characteristics of the waste waters (i.e., raw waste loads expressed as kg of pollutant per kkg of product* and attainable BOD_5 concentrations in treated waste waters from plants using technologies taken as the basis of BPCTCA) were comparable to the subcategories established for the polymers segment of the industry. The data obtained on raw waste loads and treated waste water characteristics from the plants observed and from discussions with industry representatives indicated that four major subcategories would also represent the resins segment of the industry.

Major Subcategory I - Low raw waste load (less than 10 units/1000 units of product); attainable low BOD_5 concentration (less than 20 mg/liter).

Major Subcategory II - High raw waste load (greater than 10 units/1000 units of product); attainable low BOD_5 concentration.

Major Subcategory III - High or low raw waste load; attainable medium BOD_5 concentration (in the 30-75 mg/liter range).

Major Subcategory IV - High or low raw waste load; attainable high BOD_5 concentration (over 75 mg/liter).

The attainable BOD_5 concentration in the effluent is influenced by both treatability and, for a specific waste water treatment plant design, by variations in the influent concentrations.

In Major Subcategory I where reported BOD_5 raw waste loads are less than 10 units/1000 units of product and where hydraulic flows ranged from 0.4 to 153 cu m/kkg (55 to 18,300 gal/1000 lb), the influent concentrations ranged from 8 to 720 mg/liter. While the influent concentrations varied over a 90-fold range, the effluent concentrations varied over a 3-fold range, i.e., 8 to 25 mg/liter. This indicates that practicable waste water treatment plants should be capable of retaining effluent concentrations in the vicinity of 15 mg/liter when using properly designed and well operated biological systems.

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* Production basis for establishing the unit effluent guidelines has been on the basis of actual production, not rated capacity of a plant.

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The plants in Major Subcategory II are characterized by high raw waste loads, but the waste waters can be treated to low attainable BOD$_5$ concentrations. Hydraulic flows varied from 14.2 to 116 cu m/kkg (1700 to 14,000 gal./1000 lbs). Influent concentrations of from approximately 600 to 4,300 mg/liter were reported. Although only one treatment plant was found in Category II and this was producing effluent concentrations of approximately 25 mg/liter, it is known that the waste waters from the other processes are readily treated by biological methods.

Major Subcategory III plants are characterized by high raw waste loads and observed flows from 0 to 170 cu m/kkg (0 to 20,400 gal./1000 lbs). Influent BOD$_5$ concentrations from 0 to 45,000 mg/liter were found, and effluent concentrations varied from 15 to 80 mg/liter indicating intermediate treatability of the waste waters. One of the waste water treatment facilities attained a BOD$_5$ removal of about 97 percent in a four-stage aeration basin indicating that medium BOD$_5$ concentrations are achievable.

Major Subcategory IV facilities have high raw waste loads with concentrations reported to be 2,200 mg/liter at flows of from 7 to 40 cu m/kkg (900 to 4,800 gal./1000 lbs).

Estimates of BOD$_5$ concentrations from a one-stage biological system were in the vicinity of 225 mg/liter. The supposition is made that practicable waste water treatment technology, e.g., two-stage biological treatment, might reduce the effluent concentration of Category IV processes to levels comparable with the plants appearing in Major Subcategory III; however, attainable BOD$_5$ concentrations below these levels have not been documented. Table VII-3 summarizes the performance of observed waste water treatment plants.

Additional subcategorization within the above major subcategories was necessary to account for the waste water generation which is specific to the individual products and their various processing methods. The separation of each individual product into separate subcategories simplifies the application of the effluent limitations guidelines and standards of performance by providing a clearly defined context for application of the numerical values. The advantages of this subcategorization appear to outweigh technical advantages that might be connected with product group characterization alone. The resulting major subcategories and component product subcategories are summarized in Table IV-1.

TABLE IV-1

INDUSTRY SUBCATEGORIZATION

Major Subcategory I	Major Subcategory II	Major Subcategory III	Major Subcategory IV
Ethylene-vinyl acetate copolymers	Acrylic resins	Alkyds and unsaturated polyester resins	Nitrile barrier resins
Polytetrafluoroethylene	Cellulose derivatives	Cellulose nitrate	Spandex fibers
Polypropylene fibers		Polyamids (Nylon 6/12)	
Polyvinylidene chloride		Polyesters (thermplastic)	
		Polyvinylbutyral	
		Silicones	

Several other methods for subcategorizing the industry were considered. These included plant size, plant age, raw materials and products, and air pollution and solid waste generation. The utilization of municipal systems was considered as a method of characterization for the alkyd molding and unsaturated polyesters category, however, since the waste waters are generally accepted into municipal systems and since pretreatment standards would be applicable, it was decided to establish a guidelines limitation as though the plants were treating waste waters in private waste water treating facilities. The age of the plants in this industry are determined largely by obsolescence due to size or process changes and not physical age. Similar raw materials are often used to make dissimilar products. The impact of air pollution control systems using water scrubbing and the disposal of solid wastes are not sufficient to warrant segmentation. For these reasons none of the aforementioned factors was judged to have sufficient relationships with raw waste load generation or effluent compositions to warrant their use as a basis of categorization.

SECTION V

WASTE CHARACTERIZATION

The general process flow diagrams in Section III indicate the major waste water generation points for individual processes where information could be obtained. Flow rates and compositions of process waste water streams at points of origin were not available since the companies surveyed have rarely monitored these streams except where excessive losses of a particular component have been of concern, such as in the waste waters from a distillation unit. Not only do waste water streams emanate from direct process operations, from chemical reaction by-products and other contacts, but also a significant portion of waste waters may come from the washdown of process vessels - especially where batch operations are preeminent as in the synthetic polymers industry - from area housekeeping, utilities blowdown and other sources such as laboratories and so on.

Raw Waste Loads

Raw waste water flow ranges are shown in Table V-1, and waste loads of BOD_5, COD, and suspended solids are shown in Table V-2. These data are based on information provided by the companies contacted during the course of this study. Much of the data was provided as units per unit of production by the manufacturers and was not obtained from daily production rates and waste water flows and concentrations. Furthermore, it is known that much of the data on waste water flows and raw waste loads has been derived from limited numbers of samples over short time periods. Because the synthetic polymers industry is based to a large extent on batch production methods and often on the commercial need to produce a large number of product types of a basic polymeric material, the waste water flows and raw waste loads per unit of production were reported to vary from essentially no water use (water leaves with product or no water is used in manufacture) to nearly 300 cu meters/kkg (36,000 gal./1000 lbs). The major pollutant parameters for which data were obtained are BOD_5, COD, and suspended solids. Inspection of the ranges recorded in Table V-2 shows that these pollutants vary by factors of up to 30 from low to high values for an individual polymer.

Other pollutants which may occur in the waste water from various polymer manufacturing processes are listed in Table V-3. These elements, compounds, and characteristics were developed from information obtained from industrial

TABLE V-1

WASTEWATER LOADING FOR SYNTHETIC POLYMERS PRODUCTION

	Observed or Reported Ranges of Wastewater Loading	
	(gal/1000#)	(cu m/kkg)
Acrylic resins	1700 - 5600	14.2 - 46.7
Alkyd molding compounds and unsaturated polyester resins	38 - 1440	0.3 - 12.0
Cellulose derivatives	1700 - 14000	14.2 -116.8
Cellulose nitrate	13300 - 20400	110.9 -170.2
Ethylene-vinyl acetate copolymers	275 - 300	2.3 - 2.5
Fluorocarbon polymers	2200 - 18300	18.4 -152.7
Nitrile barrier resins	900 - 4700	7.5 - 39.2
Polyamides	N.A.	N.A.
Polyester resins (thermoplastic)	260 - 770	2.2 - 6.4
Polypropylene fibers	160 - 3700	1.3 - 30.9
Polyvinyl butyral	7800 - 14200	65.1 -118.5
Polyvinyl ethers	0 - 6250	0 - 52.2
Polyvinylidene chlorides	500(E)	4.2(E)
Silicones	1000 - 33500	8.3 -279.5
Spandex fibers	1000 - 1700	8.3 - 14.2

NA = Not available

E = Estimated

TABLE V-2

SYNTHETIC POLYMERS PRODUCTION RAW WASTE LOADS

(All units expressed as kg/kkg (lb/1000 lbs of production)

	Observed, Reported, or Estimated (E) Ranges of Average Waste Loads		
	BOD_5	COD	SS
Acrylic resins	2 - 30	3 - 55	5 - 10
Alkyd molding compounds and unsaturated polyester resins	9 - 25	15 - 80	1 - 2
Cellulose derivatives	140 - 220	340 - 950	1 - 42
Cellulose nitrate	55 - 110(E)	75 - 275(E)	35(E)
Ethylene vinyl acetate copolymers	0.44 - 4.4(E)	0.2 - 54(E)	0 - 4.1
Fluorocarbon polymers	0 - 6.6(E)	4.4 - 44(E)	2.2 - 6.6(E)
Nitrile barrier resins	5 - 10(E)	10 - 30(E)	3 - 10(E)
Polyamides	NA	NA	NA
Polyester resins (thermoplastic)	0 - 10	1 - 30	NA
Polypropylene fibers	0.4 - 1.1(E)	1.8 - 2.6(E)	0.2 - 2.2(E)
Polyvinyl butyral	30 - 200	40 - 400	NA
Polyvinyl ethers	NA	10(E) - 40(E)	NA
Polyvinylidene chlorides	0(E)	8(E)	0.2(E)
Silicones	5 - 110	15 - 200	50(E)
Spandex fibers	20(E)	40(E)	NA

E = Estimated
NA = Not available

representatives, literature sources, Corps of Engineers Permit Applications for a number of plants in the plastics and synthetics industry, reviews with personnel in Regional EPA offices, and internal industrial consultants.

TABLE V-3

OTHER ELEMENTS, COMPOUNDS AND PARAMETERS

pH
Color
Turbidity
Alkalinity
Temperature
Nitrogenous Compounds (organic, ammonia and nitrates)
Oils and Greases
Dissolved Solids - principally inorganic chemicals
Phosphates
Phenolic Compounds
Sulfides
Cyanides
Fluorides
Mercury
Chromium
Copper
Lead
Zinc
Iron
Cobalt
Cadmium
Manganese
Aluminum
Magnesium
Molybdenum
Nickel
Vanadium
Antimony
Numerous Organic Chemicals

SECTION VI

SELECTION OF POLLUTANT PARAMETERS

The selection of pollutant parameters for the purpose of effluent limitations guidelines and standards of performance was based on the following general criteria:

a. Sufficient data on a parameter known to have deleterious effects in the environment were available for all of the product subcategories with regard to the raw waste load and the observed degree of removal with demonstrated technology.

b. The parameter is present in the raw waste load for an individual product subcategory in sufficient quantity to cause known deleterious effects in the environment and there is demonstrated technology available to remove the parameter.

Selected Parameters

The following parameters have been selected for the purpose of establishing recommended effluent limitations guidelines and standards of performance based on the criteria discussed above.

BOD_5

Biochemical oxygen demand (BOD) is a measure of the oxygen consuming capabilities of organic matter. The BOD does not in itself cause direct harm to a water system, but it does exert an indirect effect by depressing the oxygen content of the water. Sewage and other organic effluents during their processes of decomposition exert a BOD, which can have a catastrophic effect on the ecosystem by depleting the oxygen supply. Conditions are reached frequently where all of the oxygen is used and the continuing decay process causes the production of noxious gases such as hydrogen sulfide and methane. Water with a high BOD indicates the presence of decomposing organic matter and subsequent high bacterial counts that degrade its quality and potential uses.

Dissolved oxygen (DO) is a water quality constituent that, in appropriate concentrations, is essential not only to keep organisms living but also to sustain species reproduction, vigor, and the development of populations. Organisms undergo stress at reduced DO concentrations that make them

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less competitive and able to sustain their species within the aquatic environment. For example, reduced DO concentrations have been shown to interfere with fish population through delayed hatching of eggs, reduced size and vigor of embryos, production of deformities in young, interference with food digestion, acceleration of blood clotting, decreased tolerance to certain toxicants, reduced food efficiency and growth rate, and reduced maximum sustained swimming speed. Fish food organisms are likewise affected adversely in conditions with suppressed DO. Since all aerobic aquatic organisms need a certain amount of oxygen, the consequences of total lack of dissolved oxygen due to a high BOD can kill all inhabitants of the affected area.

If a high BOD is present, the quality of the water is usually visually degraded by the presence of decomposing materials and algae blooms due to the uptake of degraded materials that form the foodstuffs of the algal populations.

COD

Chemical oxygen demand (COD) provides a measure of the equivalent oxygen required to oxidize the materials present in a waste water sample under acid conditions with the aid of a strong chemical oxidant, such as potassium dischromate, and a catalyst (silver sulfate). One major advantage of the COD test is that the results are available normally in less than three hours. Thus, the COD test is a faster test by which to estimate the maximum oxygen exertion demand a waste can make on a stream. However, one major disadvantage is that the COD test does not differentiate between biodegradable and nonbiodegradable organic material. In addition, the presence of inorganic reducing chemicals (sulfides, reducible metallic ions, etc.) and chlorides may interfere with the COD test. As a rough generalization, it may be said that pollutants which would be measured by the BOD_5 test will also show up under the COD test, but that additional pollutants which are more resistant to biological oxidation (refractory) will also be measured as COD.

Total Suspended Solids

Suspended solids include both organic and inorganic materials. The inorganic components include sand, silt, and clay. The organic fraction includes such materials as grease, oil, tar, animal and vegetable fats, various fibers, sawdust, hair, and various materials from sewers. These solids may settle out rapidly and bottom deposits are often a mixture of both organic and inorganic solids. They adversely affect fisheries by covering the bottom of the stream or lake with a blanket of material that destroys the fishfood bottom fauna or the spawning ground of fish. Deposits containing organic materials may deplete bottom oxygen supplies and produce hydrogen sulfide, carbon dioxide, methane, and other noxious gases.

In raw water sources for domestic use, state and regional agencies generally specify that suspended solids in streams shall not be present in sufficient concentration to be objectionable or to interfere with normal treatment processes. Suspended solids in water may interfere with many industrial processes and cause foaming in boilers, or encrustations on equipment exposed to water, especially as the temperature rises. Suspended solids are undesirable in water for textile industries; paper and pulp; beverages; dairy products; laundries; dyeing; photography; cooling systems; and power plants. Suspended particles also serve as a transport mechanism for pesticides and other substances which are readily sorbed into or onto clay particles.

Solids may be suspended in water for a time, and then settle to the bed of the stream or lake. These settleable solids discharged with man's wastes may be inert, slowly biodegradable materials, or rapidly decomposable substances. While in suspension, they increase the turbidity of the water, reduce light penetration, and impair the photosynthetic activity of aquatic plants.

Solids in suspension are aesthetically displeasing. When they settle to form sludge deposits on the stream or lake bed, they are often much more damaging to the life in water, and they retain the capacity to displease the senses. Solids, when transformed to sludge deposits, may do a variety of damaging things, including blanketing the stream or lake bed and thereby destroying the living spaces for those benthic organisms that would otherwise occupy the habitat. When of an organic and therefore decomposable nature, solids use a portion or all of the dissolved oxygen available in the area. Organic materials also serve as a seemingly inexhaustible food source for sludgeworms and associated organisms.

Turbidity is principally a measure of the light absorbing properties of suspended solids. It is frequently used as a substitute method of quickly estimating the total suspended solids when the concentration is relatively low.

pH, Acidity and Alkalinity

Acidity and alkalinity are reciprocal terms. Acidity is produced by substances that yield hydrogen ions upon hydrolysis and alkalinity is produced by substances that yield hydroxyl ions. The terms "total acidity" and "total alkalinity" are often used to express the buffering capacity of a solution. Acidity in natural waters is caused by carbon dioxide, mineral acids, weakly dissociated acids, and the salts of strong acids and weak bases. Alkalinity is caused by strong bases and the salts of strong alkalies and weak acids.

The term pH is a logarithmic expression of the concentration of hydrogen ions. At a pH of 7, the hydrogen and hydroxyl ion concentrations are essentially equal and the water is neutral. Lower pH values indicate acidity while higher values indicate alkalinity. The relationship between pH and acidity or alkalinity is not necessarily linear or direct.

Waters with a pH below 6.0 are corrosive to water works structures, distribution lines, and household plumbing fixtures and can thus add such constituents to drinking water as iron, copper, zinc, cadmium, and lead. The hydrogen ion concentration can affect the "taste" of the water. At a low pH water tastes "sour." The bactericidal effect of chlorine is weakened as the pH increases, and it is advantageous to keep the pH close to 7. This is very significant for providing safe drinking water.

Extremes of pH or rapid pH changes can exert stress conditions or kill aquatic life outright. Dead fish, associated algal blooms, and foul stenches are aesthetic liabilities of any waterway. Even moderate changes from "acceptable" criteria limits of pH are deleterious to some species. The relative toxicity to aquatic life of many materials is increased by changes in the water pH. Metalocyanide complexes can increase a thousand-fold in toxicity with a drop of 1.5 pH units. The availability of many nutrient substances varies with the alkalinity and acidity. Ammonia is more lethal with a higher pH.

The lacrimal fluid of the human eye has a pH of approximately 7.0 and a deviation of 0.1 pH unit from the norm may result in eye irritation for the swimmer. Appreciable irritation will cause severe pain.

Other Pollutant Parameters

The quantitative identification of other pollutants from analytical data was impossible to establish. However, the following are identified as the major other pollutants or parameters which may have to be considered in the National Pollution Discharge Elimination System permits.

Phenolic Compounds

Phenols and phenolic wastes are derived from petroleum, coke, and chemical industries; wood distillation; and domestic and animal wastes. Many phenolic compounds are more toxic than pure phenol; their toxicity varies with the combinations and general nature of total wastes. The effect of combinations of different phenolic compounds is cumulative.

Phenols and phenolic compounds are both acutely and chronically toxic to fish and other aquatic animals. Also, chlorophenols produce an unpleasant taste in fish flesh that destroys their recreational and commercial value.

It is necessary to limit phenolic compounds in raw water used for drinking water supplies, as conventional treatment methods used by water supply facilities do not remove phenols. The ingestion of concentrated solutions of phenols will result in severe pain, renal irritation, shock, and possibly death.

Phenols also reduce the utility of water for certain industrial uses, notably food and beverage processing, where it creates unpleasant tastes and odors in the product.

Nitrogenous Compounds

Nitrogenous compounds can occur as a result of biological activity in the waste water treatment and can also come from manufacturing processes such as urea, melamine, nylon, ABS/SAN, cellulose nitrate, cellulose derivatives, nitrile barrier resins, and acrylics. Ammonia is a common product of the decomposition of organic matter. Dead and decaying animals and plants along with human and animal body wastes account for much of the ammonia entering the aquatic ecosystem. Ammonia exists in its non-ionized form only at higher pH levels and is the most toxic in this state. The lower the pH, the more ionized ammonia is formed and its toxicity decreases. Ammonia, in the presence of dissolved oxygen, is converted to nitrate (NO_3) by nitrifying bacteria. Nitrite (NO_2), which is an intermediate product between ammonia and nitrate, sometimes occurs in quantity when depressed oxygen conditions permit. Ammonia can exist in several other chemical combinations including ammonium chloride and other salts.

Nitrates are considered to be among the poisonous ingredients of mineralized waters, with potassium nitrate being more poisonous than sodium nitrate. Excess nitrates cause irritation of the mucous linings of the gastrointestinal tract and the bladder; the symptoms are diarrhea and diuresis, and drinking one liter of water containing 500 mg/l of nitrate can cause such symptoms.

Infant methemoglobinemia, a disease characterized by certain specific blood changes and cyanosis, may be caused by high nitrate concentrations in the water used for preparing feeding formulae. While it is still impossible to state precise concentration limits, it has been widely recommended that water containing more than 10 mg/l of nitrate nitrogen (NO_3-N) should not be used for infants. Nitrates are also harmful in fermentation processes and can cause disagreeable tastes in beer. In most natural water the pH range is such that ammonium ions (NH_4^+) predominate. In alkaline waters, however, high concentrations of un-ionized ammonia in undissociated ammonium hydroxide increase the toxicity of ammonia solutions. In streams polluted with sewage, up to one-half of the nitrogen in the sewage may be in the form of free ammonia, and sewage may carry up to 35 mg/l of total nitrogen. It has been shown that at a level of 1.0 mg/l un-ionized ammonia, the ability of hemoglobin to combine with oxygen is impaired and fish may suffocate. Evidence indicates that ammonia exerts a considerable toxic effect on all aquatic life within a range of less than 1.0 mg/l to 25 mg/l, depending on the pH and dissolved oxygen level present.

Ammonia can add to the problem of eutrophication by supplying nitrogen through its breakdown products. Some lakes in warmer climates, and others that are aging quickly are sometimes limited by the nitrogen available. Any increase will speed up the plant growth and decay process.

Fluorides

As the most reactive non-metal, fluorine is never found free in nature but as a constituent of fluorite or fluorspar, calcium fluoride, in sedimentary rocks and also of cryolite, sodium aluminum fluoride, in igneous rocks. Owing to their origin only in certain types of rocks and only in a few regions, fluorides in high concentrations are not a common constituent of natural surface waters, but they may occur in detrimental concentrations in ground waters.

Fluorides are used as insecticides, for disinfecting brewery apparatus, as a flux in the manufacture of steel, for preserving wood and mucilages, for the manufacture of glass and enamels, in chemical industries, for water treatment, and for other uses.

Fluorides in sufficient quantity are toxic to humans, with doses of 250 to 450 mg giving severe symptoms or causing death.

There are numerous articles describing the effects of fluoride-bearing waters on dental enamel of children; these studies lead to the generalization that water containing less than 0.9 to 1.0 mg/l of fluoride will seldom cause mottled enamel in children, and for adults, concentrations less than 3 or 4 mg/l are not likely to cause endemic cumulative fluorosis and skeletal effects. Abundant literature is also available describing the advantages of maintaining 0.8 to 1.5 mg/l of fluoride ion in drinking water to aid in the reduction of dental decay, especially among children.

Chronic fluoride poisoning of livestock has been observed in areas where water contained 10 to 15 mg/l fluoride. Concentrations of 30 - 50 mg/l of fluoride in the total ration of dairy cows is considered the upper safe limit. Fluoride from waters apparently does not accumulate in soft tissue to a significant degree and it is transferred to a very small extent into the milk and to a somewhat greater degree into eggs. Data for fresh water indicate that fluorides are toxic to fish at concentrations higher than 1.5 mg/l.

Phosphates

Surfactants may be used in the proprietary formulations of a number of manufacturing processes such as polypropylene fibers, acrylic resins, nitrile barrier resins, thermoplastic polyesters, polyvinylidene chloride, and so on. During the past 30 years, a formidable case has developed for the belief that increasing standing crops of aquatic plant growths, which often interfere with water uses and are nuisances to man, frequently are caused by increasing supplies of phosphorus. Such phenomena are associated with a condition of accelerated eutrophication or aging of waters. It is generally recognized that phosphorus is not the sole cause of eutrophication, but there is evidence to substantiate that it is frequently the key element in all of the elements required by fresh water plants and is generally present in the least amount relative to need. Therefore, an increase in phosphorus allows use of other, already present, nutrients for plant growths. Phosphorus is usually described, for this reason, as a "limiting factor."

When a plant population is stimulated in production and attains a nuisance status, a large number of associated liabilities are immediately apparent. Dense populations of pond weeds make swimming dangerous. Boating and water skiing and sometimes fishing may be eliminated because of the mass of vegetation that serves as an physical impediment to such activities. Plant populations have been associated with stunted fish populations and with poor fishing. Plant nuisances emit vile stenches, impart tastes and odors to water supplies, reduce the efficiency of industrial and municipal water treatment, impair aesthetic beauty, reduce or restrict resort trade, lower waterfront property values, cause skin rashes to man during water contact, and serve as a desired substrate and breeding ground for flies.

Phosphorus in the elemental form is particularly toxic, and subject to bioaccumulation in much the same way as mercury. Colloidal elemental phosphorus will poison marine fish (causing skin tissue breakdown and discoloration). Also, phosphorus is capable of being concentrated and will accumulate in organs and soft tissues. Experiments have shown that marine fish will concentrate phosphorus from water containing as little as 1 ug/l.

Oils and Greases

Although oils and greases are most frequently found to occur as the result of equipment leaks and so on, and are not usually of significant concern to this industry, some manufacturing processes such as are used to produce silicones, polypropylene, and spandex fibers may require that oil and grease be considered a parameter.

Oil and grease exhibit an oxygen demand. Oil emulsions may adhere to the gills of fish or coat and destroy algae or other plankton. Deposition of oil in the bottom sediments can serve to exhibit normal benthic growths, thus interrupting the aquatic food chain. Soluble and emulsified material ingested by fish may taint the flavor of the fish flesh. Water soluble components may exert toxic action on fish. Floating oil may reduce the re-aeration of the water surface and in conjunction with emulsified oil may interfere with photosynthesis. Water insoluble components damage the plumage and coats of water animals and fowls. Oil and grease in a water can result in the formation of objectionable surface slicks preventing the full aesthetic enjoyment of the water.

Oil spills can damage the surface of boats and can destroy the aesthetic characteristics of beaches and shorelines.

Dissolved Solids

Dissolved inorganic salts are an integral part of the operation of many processes. Although no effluent guidelines have been established for dissolved solids, receiving stream water quality standards should determine if limitations are necessary. Manufacturing processes for the following products are believed to produce the greatest loads of dissolved solids:

Acrylic resins
Cellulose derivatives
Cellulose nitrate
Polytetrafluoroethylene
Silicones

In natural waters the dissolved solids consist mainly of carbonates, chlorides, sulfates, phosphates, and possibly nitrates of calcium, magnesium, sodium, and potassium, with traces of iron, manganese, and other substances.

Many communities in the United States and in other countries use water supplies containing 2000 to 4000 mg/l of dissolved salts, when no better water is available. Such waters are not palatable, may not quench thirst, and may have a laxative action on new users. Waters containing more than 4000 mg/l of total salts are generally considered unfit for human use, although in hot climates such higher salt concentrations can be tolerated whereas they could not be in temperate climates. Waters containing 5000 mg/l or more are reported to be bitter and act as bladder and intestinal irritants. It is generally agreed that the salt concentration of good, palatable water should not exceed 500 mg/l.

Limiting concentrations of dissolved solids for freshwater fish may range from 5,000 to 10,000 mg/l, according to species and prior acclimatization. Some fish are adapted to living in more saline waters, and a few species of freshwater forms have been found in natural waters with a salt concentration of 15,000 to 20,000 mg/l. Fish can slowly become acclimatized to higher salinities, but fish in waters of low salinity cannot survive sudden exposure to high salinities, such as those resulting from discharges of oil-well brines. Dissolved solids may influence the toxicity of heavy metals and organic compounds to fish and other aquatic life, primarily because of the antagonistic effect of hardness on metals.

Waters with total dissolved solids over 500 mg/l have decreasing utility as irrigation water. At 5,000 mg/l water has little or no value for irrigation.

Dissolved solids in industrial waters can cause foaming in boilers and cause interference with cleanliness, color, or taste of many finished products. High contents of dissolved solids also tend to accelerate corrosion.

Specific conductance is a measure of the capacity of water to convey an electric current. This property is related to the total concentration of ionized substances in water and water temperature. This property is frequently used as a substitute method of quickly estimating the dissolved solids concentration.

Toxic and Hazardous Chemicals

The industry uses a large number of accelerators and inhibitors which are considered proprietary and, consequently, no information could be obtained. Some of these compounds, especially cyanide, cadmium, and mercuric compounds, may be on EPA's recently proposed list of toxic substances as published in the Federal Register of December 27, 1973.

Alkalinity, Color, Turbidity, and the Metals Listed in Table V-3

These pollutants may be present in waste waters from selected processes in varying amounts; however, no data could be obtained which would permit establishing raw or treated waste loads. Therefore, they are listed so that appropriate cognizance can be taken to determine whether or not they are present in amounts requiring effluent limitation because of receiving water quality standards. Where appropriate the particular parameters are summarized in Table VI-1.

TABLE VI-1

OTHER ELEMENTS AND COMPOUNDS SPECIFIC TO THE RESINS SEGMENT OF PLASTICS AND SYNTHETICS INDUSTRY

Alkyd Compounds and Ester Resins	Lead Cobalt
Polytetrafluoroethylene	Fluorides
Spandex Fibers	Cyanides Oils and Grease Organic Nitrogen
Acrylic Resins	Oils and Grease
Polypropylene Fibers	Oils and Grease Phosphates
Nitrile Barrier Resins	Organic Nitrogen Cyanides
Polyamides	Organic Nitrogen
Cellulose Derivatives	Inorganic Nitrogen
Cellulose Nitrate	Inorganic Nitrogen
Silicones	Polychlorinated Organics Copper Fluorides
Polyvinylidene Chloride	Polychlorinated Organics
Polyester Resins (Thermoplastic)	Cobalt Manganese Cadmium

SECTION VII

CONTROL AND TREATMENT TECHNOLOGY

Technology for the control and treatment of waste waters from this segment of the plastics and synthetics industry is not specific to the industry but can utilize any of the broad spectrum of technologies found in waste water treatment. These technologies can be divided into the same three broad categories found in the rest of the synthetics and plastics industry. These are:

1. Presently used waste water treatment technology.
2. Potentially usable waste water treatment technology.
3. Control of waterborne pollutants by in-plant or in-process practices.

The application of presently or potentially usable waste water treatment technologies may be applied on selected bases to segregated streams or may be incorporated into a centralized waste water treatment plant. Although categories 1 and 2, often denoted as end-of-pipe treatment, may be applied regardless of the manufacturing process, in-process control to prevent pollutants from entering water streams has a great potential for reducing the load of pollutants as well as the waste water flows. The application of in-plant control technology falls into two broad categories: (1) process requirements and (2) plant practices. Process requirements for water usage depend upon the types of reactions being carried out, the amounts of unreacted raw materials or undesired by-products that must be removed by water washing to attain product specifications, the removal of catalyst activators or other additives necessary to control the reaction or create the appropriate chemical characteristics, and the use of water for quenching, creating vacuum, or other operations that contact process streams. The emission of pollutants into waste streams outside of the direct process operations may come from poor housekeeping practices or from the excessive usage of water for cleaning up spills, leaks, and accidental occurrences due to equipment failure or personnel error. Water used to control accidental occurrences or hazardous conditions, such as fires, etc., is employed very occasionally, and usually is not considered as contributing to the pollution loads in the waste waters. Recycle of

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treated waste waters for such uses as housekeeping, cooling tower makeup and fire ponds is currently being practiced in the industry. One plant reports reuse of up to 75 percent of its treated effluent. (50)

As indicated earlier, the survey found no waste water treatment technologies unique to this segment of the plastics and synthetics industry. The waste water treatment technology is similar to that found during the survey of the first segment of the industry and is generally similar to that of other industries. Obviously, application of basically similar technology, e.g., activated sludge biological treatment, often requires unique conditions for specific waste water and results in considerable variation in performance characteristics such as efficiency of pollutant removal.

Presently Used Waste Water Treatment Technology

This segment of the plastics and synthetics industry was found to have relatively few waste water treatment plants devoted solely to the treatment of the waste waters from a particular product. A major portion of the individual manufacturing plants, except in the alkyd and polyester resins categories, was visited or otherwise contacted to determine if water treatment facilities were installed. It was found that a large portion of the waste waters from the various products enter either centralized treatment facilities for multi-plant chemical complexes or municipal sewage systems. The major portion of the waste waters from the manufacture of silicones is treated or will be treated in their own waste water treatment plants. Typical operating data or design information on silicone waste water treatment plants are included in Tables VII-1 and VII-2; however, one-half of the companies requested confidential handling of the data provided and, therefore, those data are not included. In addition, confidentiality was requested by a polytetrafluoroethylene and a nitrile barrier resin manufacturer. Although a significant portion of the design and operating data shown in Tables VII-1 and VII-2 are from waste water treatment plants receiving waste waters from a number of different chemical manufacturing processes, the inclusion of data from multi-process waste water treatment plants was made to indicate the operating conditions and efficiencies found even though the load of pollutants from the particular process was a small portion of the total load on the waste water treatment plant. It must be recognized that the efficiency of pollutant removal from waste waters would not necessarily be the same as that demonstrated by the multi-process treatment plant unless the waste waters

TABLE VII-1

OPERATIONAL PARAMETERS OF WASTEWATER TREATMENT PLANTS

(Metric Units)

	Type of Plant	Methyl* Methacrylate	Polyvinyl Butyral	Thermoplastic* P/E	Acrylic*	Vinyl Acetate	EVA #1*	EVA #2*	Polypropylene	Polyvinylidene* Chloride
1	Type of Treatment	Neut, screen, equalize, cool, nutrient, bio ox, clarify, sludge aeration & centrifuging	Equal, aer lagoon coag add, clarif	Equal & neut aer lagoons	(30-70% of wastes due to acrylic mfg) equal, 2 trickling filters parallel or series clarif & polish lagoons (57 acres)	Skim, oil sep equal, bio-aer clarif w/chem add, bio-anaerobic	Skim, filter, burn recovered oil, recycle recovered polymer (primary only)	Skim, oil sep clar, anaerob bio	Skim before discharge (primary only)	Aerated lagoon settling basin
2	Hydraulic Load (cu m/day)	11,000(6800 actual)	1,135	43,906	3,936	409	4,807	30,280	1,890	4,656
3	Residence Time (hours)(1)	19+	34	120(2904)	41.5(424)	36	0.3	8760	-	-
4	BOD_5 (kg removed/day/cu m)	0.85+	0.36	0.009	0.109	1.02 (API type skimmer)		-	-	-
5	COD (kg removed/day/cu m)	-	0.46	-	-	0.58	-	-	-	-
6	Power (HP/cu m)	0.106+	0.06	0.018	-	0.007	-	40.7	-	-
7	Suspended solids (mg/liter)	50+	135	-	42	38	23	-	33	35
8	Clarifier overflow (m/day)	24.5	7.7	-	24.4 & 57.0	0.20	-	51	-	-
9	Biomass (mg/liter)	3000+	2991	-	-	1200-1800	-	-	-	-
10	BOD_5 (kg removed/day/kg MLSS)	-	0.17	-	-	-	-	-	-	-
11	Typical Values NH_3-N out (mg/liter)	-	14.6	-	1.89	-	.1 to 1.5	-	-	-
12	Typical Values TKN out (mg/liter)	-	14.8	-	8.33	-	-	-	-	-
13	BOD_5 in (mg/liter)	800+	543	1,476	1,946	1,562	-	(154)+	-	59
14	BOD_5 out (mg/liter)	120+	39.7	422	11	17	13	-	-	22
15	COD BOD_5 in	-	1.5	-	-	0.6(TOC/BOD)	-	(4.2)+	-	13
16	COD in (mg/liter)	-	839	-	-	904(TOC)	-	20,000(TOC)	-	776
17	COD out (mg/liter)	-	179	-	16	37(TOC)	47	800(TOC)	27	251
18	COD/BOD_5 out	-	4.5	-	1.45	2.2(TOC/BOD)	3.6	-	-	11.4
19	Eff. BOD_5 Removal	85+	92.7+	72+	99.4	99+	-	-	-	63+
20	Eff. COD Removal	-	79+	-	-	96+(TOC)	-	96(TOC)	-	68+

Comments:

+ Design Values

Submerged aerators horsepower calculated from size of blowers.

Notes:

* Indicates wastewater plant serves a chemical manufacturing complex.

(1) First value is residence time in aerobic biological system. Values in ( ) is residence time in total system.

TABLE VII-1
(Continued)

OPERATIONAL PARAMETERS OF WASTEWATER TREATMENT PLANTS
(Metric Units)

Type of Plant	Alkyd/Polyester Resins			Silicones			Cellulose* Nitrate	Polyvinyl Ether		Spandex	
										#1*	#2*
1 Type of Treatment	(Neut.) municipal treatment	Settling, bio-aerobic (4 stage)clarify	Municipal treatment (neut) & hold lagoon	Neut screen sedimentation screen, skim. filtration (primary only)	Neut. clarify sludge dewater basin (primary only)	Bio-aerobic, clarify (proposed secondary)	Neut. sediment spray oxidation	Equal. neut.	Settle & neut process wastes chlorinate city wastes act. sludge clarify	Biological coagulation, centrifugation	Municipal treatment
2 Hydraulic Load (cu m/day)	5.7	170	2	1,022	25,740	25,740	2.0	4,920	34,440	-	-
3 Residence Time (hours)(1)	-	252	-	-	1.3 (clarifier)	3+	8.4	-	7.5 plant 2 city	-	-
4 BOD_5 (#removed/day/cu m)	-	0.28	-	-	-	-	-	-	0.93	-	-
5 COD (#removed/day/cu m)	-	0.36	-	-	-	-	-	-	0.66	-	-
6 Power (HP/cu m)	-	0.034	-	-	-	-	0.02	-	-	-	-
7 Suspended solids (mg/liter)	-	64	-	20	100	-	40.6	60	208	120	-
8 Clarifier overflow (m/day)	-	12.7	-	-	43.2	24.4	-	-	52.3	-	-
9 Biomass (mg/liter)	-	4,000	-	-	-	6500+	-	-	-	-	-
10 BOD_5 (kg removed/day/kg MLSS)	-	0.7	-	-	-	0.04	-	-	-	-	-
11 Typical Values NH_3-N out (mg/liter)	-	(Nutrients added)	-	-	-	-	-	156	-	-	-
12 Typical Values TKN out (mg/liter)	-	-	-	1.12	-	-	-	16	-	-	-
13 BOD_5 in(mg/liter)	-	2,960	-	-	-	276+	219	-	776	2,200	3,900
14 BOD_5 out(mg/liter)	-	28	-	24	-	38+	30	1,100	104	225	-
15 COD BOD_5 in	-	1.36	-	-	-	2.5	-	-	3.05	2.1	-
16 COD in (mg/liter)	-	3,890	-	-	-	688	-	-	2,370	4,440	-
17 COD out (mg/liter)	-	146	-	13.9	-	205+	123.4	1,800	540	1,440	-
18 COD/BOD_5 out	-	5.2	-	0.58	-	5.4+	4.1+	1.6	6.2	6.4	-
19 Eff. BOD_5 Removal	-	99+	-	-	-	86.2+	86	-	84.6	73	-
20 Eff. COD Removal	-	96.2+	-	-	-	70.2+	-	-	73	65-70+	-

Comments:

+Design Values
Submerged aerators horsepower calculated from size of blowers.

Includes lagoon separator - skimmer, sump & pH controller.

Notes:

* Indicates wastewater plant serves a chemical manufacturing complex.
(1) First value is residence time in aerobic biological system. Values in ( ) is residence time in total system.

TABLE VII-2
OPERATIONAL PARAMETERS OF WASTEWATER TREATMENT PLANTS
(English Units)

Type of Plant	Methyl* Methacrylate	Polyvinyl Butyral	Thermoplastic* P/E	Acrylic*	Vinyl Acetate	EVA #1	EVA #2	Polypropylene	Polyvinylidene* Chloride
1 Type of Treatment	Neut, screen, equalize, cool, nutrient, bio ox, clarify, sludge aeration & centrifuging	Equal, aer lagoon coag add, clarif	Equal & neut, aer lagoons	(30-70% of wastes due to acrylic mfg) equal, 2 trickling filters parallel or series clarif & polishing lagoons (57 acres)	Skin, oil sep equal, bio-aer clarif w/chem add, bio-anaerobic	Skin, filter, burn recoverd oil, recycle recovered polymer (primary only)	Skin, oil sep clar, anaerob bio	Skim before discharge (primary only)	Aerated lagoon settling basin
2 Hydraulic Load (MGD)	2.9+ (1.8 actual)	0.3	11.6	1.04	0.108	1.27	8	0.5	1.23 MGD
3 Residence Time (hours)(1)	19+	34	120(2904)	41.5(424)	36	0.3	8,760	-	-
4 BOD_5 (#removed/day/1000 ft^3)	53+	22	0.54	6.8	64	(API type skimmer)	-	-	-
5. COD (#removed/day/1000 ft^3)	-	29	-	-	36(TOC)	-	-	-	-
6 Power (HP/1000 ft^3)	3.0	1.7	0.5	-	0.2	-	-	-	-
7 Suspended solids (mg/liter)	50+	135	-	42	28	23	-	33	35
8 Clarifier overflow (GPD/ft^2)	600+	189	-	600 & 1400	5	-	1,257	-	-
9 Biomass (mg/liter)	3,000+	2,991	-	-	1200-1800	-	-	-	-
10 BOD_5 (# removed/day/#MLSS)	0.23	0.17	-	-	-	-	-	-	-
11 Typical Values NH_3-N out (mg/liter)	-	14.6	-	1.89	-	.1 to 1.5	-	-	-
12 Typical Values TKN out (mg/liter)	-	14.8	-	8.33	-	-	-	-	-
13 BOD_5 in (mg/liter)	800+	543	1,476	1,946		-	(154)+	-	59
14 BOD_5 out (mg/liter)	120+	39.7	422	11	17	13	-	-	22
15 COD/BOD_5 in	-	1.5	-	-	0.6(TOC/BOD)	-	(4.2)+	-	13
16 COD in (mg/liter)	-	839	-	-	904(TOC)	-	20,000(TOC)	-	776
17 COD out (mg/liter)	-	179	-	16	37(TOC)	47	800(TOC)	27	231
18 COD/BOD_5 out	-	4.5	-	1.45	2.2(TOC/BOD)	3.6	-	-	11.4
19 Eff. BOD_5 Removal	85+	92.7+	71+	99.4	99+	-	-	-	63+
20 Eff. COD Removal	-	79+	-	-	96+(TOC)	-	96(TOC)	-	68+

Comments: + Design value

Submerged aerators horsepower calculated from size of blowers.

Notes: * Indicates wastewater plant serves a chemical manufacturing complex.

(1) First value is residence time in aerobic biological system. Values in ( ) is residence time in total system.

TABLE VII-2
(Continued)

OPERATIONAL PARAMETERS OF WASTEWATER TREATMENT PLANTS
(English Units)

Type of Plant	Alkyd/Polyester Resins			Silicones			Cellulose* Nitrate		Polyvinyl Ether	Spandex #1	Spandex #2
1 Type of Treatment	(Neut.) Municipal treatment	Settling, aerobic (4 stage) clarify	Municipal treatment (neut.) & hld lagoon	Neut screen sedimentation screen, skim. filtration (primary only)	Neut. clarify sludge dewater basin (primary only)	[illegible]-aerobic, clarify (proposed secondary)	Neut. sediment spray oxidation	Equal. neut	Settle & neut process wastes chlorinate city wastes act. sludge clarify	Biological coagulation centrifugation	Municipal treatment
2 Hydraulic Load (MGD)	0.0015	0.045	0.00053	0.27	6.8	6.8	2.0	1.3	9.1	-	-
3 Residence Time (hours)(1)	-	252	-	-	1.3 (clarifier)	3+	8.4	-	7.5 plant 2 city	-	-
4 BOD_5 (#removed/day/1000 cu ft)	-	17.4	-	-	-	-	-	-	58	-	-
5 COD (#removed/day/1000 cu ft)	-	22.2	-	-	-	-	-	-	41	-	-
6 Power (HP/1000 cu ft)	-	0.95	-	-	-	-	0.6	-	-	-	-
7 Suspended solids (mg/liter)	-	64	-	20	100	-	40.6	60	208	120	-
8 Clarifier overflow (m/day)	-	312.5	-	-	1,060	600+	-	-	1,283	-	-
9 Biomass (mg/liter)	-	4,000	-	-	-	6,500+	-	-	-	-	-
10 BOD_5 (# removed/day/ # MLSS)	-	0.7	-	-	-	0.04	-	-	-	-	-
11 Typical Values NH_3-N out (mg/liter)	-	(Nutrients added)	-	-	-	-	-	156	-	-	-
12 Typical Values TKN out (mg/liter)	-	-	-	1.12	-	-	-	16	-	-	-
13 BOD_5 in (mg/liter)	-	2,960	-	-	-	276+	219	-	776	2,200	3,900
14 BOD_5 out (mg/liter)	-	28	-	24	-	38+	30	1,100	104	225	-
15 COD BOD_5 in	-	1.36	-	-	-	2.5	-	-	3.05	2.1	-
16 COD in (mg/liter)	-	3,890	-	-	-	688	-	-	,370	4,400	-
17 COD out (mg/liter)	-	146	-	13.9	-	205+	123.4	1,800	640	1,440	-
18 COD/BOD_5 out	-	5.2	-	0.58	-	5.4+	4.1+	1.6	6.2	6.4	-
19 Eff. BOD_5 Removal	-	99+	-	-	-	86.2+	86	-	86.6	90+	-
20 Eff. COD Removal	-	96.2+	-	-	-	70.2+	-	-	79	65-70+	-

Comments: + Design Values

Submerged aerators horsepower calculated from size of blowers.

Includes lagoon separator - skimmer, sump & pH controller.

Notes: *Indicates wastewater plant serves a chemical manufacturing complex.

(1) First value is residence time in aerobic biological system. Values in ( ) is residence time in total system.

TABLE VII-3

PERFORMANCE OF OBSERVED WASTEWATER TREATMENT PLANTS

	BOD_5		COD		Suspended Solids	
	Inlet mg/liter	Outlet mg/liter	Inlet mg/liter	Outlet mg/liter	Inlet mg/liter	Outlet mg/liter
Major Subcategory I						
Ethylene-Vinyl Acetate*	-	-	20,000(TOC)	800(TOC)	-	-
Ethylene-Vinyl Acetate*	-	10	-	48	-	21
Fluorocarbons	-	-	-	-	-	-
Polypropylene Fibers	-	8	-	27	-	-
Polyvinylidene Chloride*	59	22	776	251	-	360
Major Subcategory II						
Acrylic Resins*	630	17	-	24	-	42
Acrylic Resins**	666	66	-	-	-	-
Cellulose Derivatives	-	-	-	-	-	-
Polyvinyl Butyral	543	40	839	179	-	135
Major Subcategory III						
Alkyds & Unsat. Polyesters	2960	28	3890	146	-	64
Cellulose Nitrate	251	34	-	124	-	41
Polyamids (Nylon 6/12 only)	-	-	-	-	-	-
Polyesters (Thermoplastic)*	1476	422	-	-	-	-
Polyvinyl Ethers***	776	104	2370	640	-	208
Silicones**	276	38	688	205	-	-
Major Subcategory IV						
Nitrile Barrier Resins	-	-	-	-	-	-
Spandex*	2200	225	4400	1440	-	120

* Part of a multi-plant wastewater treatment facility ; Polyester operations contribute app. 14% of the loading

** Design values - facility not operable at time of visit

*** Combined industrial municipal treatment facility

TABLE VII-4

OBSERVED TREATMENT AND AVERAGE EFFLUENT LOADINGS FROM WASTE WATER TREATMENT PLANT INSPECTIONS

Product	Acrylic Resins	Acrylic Resins	Alkyds and Unsaturated Polyester	Cellulose Nitrate*	Ethylene-Vinyl Acetate*	Polypropylene Fibers	Polyvinyl Butyral	Silicones	
Control and Treatment Technology Currently in Use	Equalization, Trickling Filters - Polishing Lagoons	Neutralization, Equalization Bio-oxidation (design)	Settling. Four-Stages of Bio-oxidation	Neutralization, Sedimentation Spray Oxidation	Skimming Bio-oxidation	Skimming Only	Equalization, Activated Sludge	(Multi-Product) Neutralization Bio-oxidation (design)	(Fluid Product) Neutralization Sedimentation Skimming, Filtration
				Observed or Reported Effluent Loading					
[kg/kkg (lbs/1000) of Product]									
BOD_5	0.70	3.1	0.09	3.34	0.07	0.24	2.6	8.6	1.1
COD		30.8	0.47	13.7	0.25	0.78	13.6	46.0	-
Suspended Solids			0.21	4.4	0.15	0.98	6.5	25.0	1.1

*Multi-plant wastewater treatment facility represented the major portion of the hydraulic and pollutant load. Because of the many variables that can influence performance of a waste water treatment plant, the performance of a multi-process waste water treatment plant can only be taken as a qualitative indicator of the removal efficiency that might be achieved when operating exclusively on the waste waters from a single process. The paucity of data on waste water treatment facilities, as recorded in Tables VII-1, VII-2, VII-3, and VII-4, for this segment of the industry is not surprising because of the relatively small production capacities of the products and the use of municipal sewerage systems or multi-process waste water treatment plants.

Biological treatment of the waste waters from this segment of the industry appears to be the method chosen for effecting removal of soluble substances. Pretreatment before biological systems is often required whether the biological system is operated by the manufacturer or is a municipal sewage treatment plant. This treatment is predominantly neutralization for the control of pH prior to biological treatment. Primary treatment such as required in municipal treatment plants is not routinely necessary for these waste waters; however, when significant amounts of oils or solvents do occur, the use of oil separators, skimmers, and settling basins or lagoons is used.

The effectiveness of a particular operational mode of the biological processes for removal of biologically degradable pollutants varies widely depending upon the characteristics of the waste waters being treated. Consequently, it is impossible to generalize regarding the operating conditions applied in biological treatment other than to say that these are based on well understood principles. The design and operational characteristics of the biological waste water treatment plants are paramount in determining the overall success in removing biologically degradable pollutants. Operational parameters found for waste water treatment plants in this segment of the plastics and synthetics industry were generally within the range found earlier and reported in EPA Document 440/1-73/010 (16). These are recorded in Tables VII-1 and VII-2. Similar removal efficiencies for COD were found and the ratios of COD/BOD$_5$ were within the earlier ranges.

The applicability and limitation of biological treatment processes as well as physico-chemical processes to this segment of the plastics and synthetics industry are the same as outlined for the first segment and will be found in Section VII of EPA Document 440/1-73/010 (16).

Copper

The most widely accepted and economically feasible method for the removal of relatively low concentrations of soluble copper from waste water streams is precipitation followed by sedimentation and filtration.

Under alkaline conditions, copper will tend to precipitate out of solution and form solid particles composed of the various oxides, hydroxides, and carbonates of copper. Alkaline conditions are generally accomplished by the addition of lime to the waste water. Typically, a solids-recirculation clarifier is employed to promote the formation, growth, and sedimentation of the precipitated particles. Coagulants were often added to the waste water in order to encourage the agglomeration of precipitated particles to such a size where they may readily settle.

The theoretical minimum solubility for copper in the pH range employed in the lime treatment process is on the order to 0.01 mg/liter, but this level is seldom attained due to slow reaction rates, poor separation of colloidal precipitates, and the influence of other ions in solution. Most reported effluent copper concentrations from the lime precipitation process are on the order to 0.5 to 1.0 mg/liter. If lime precipitation is followed by filtration, concentrations on the order of 0.25 mg/liter are attainable.

Lower levels can be achieved by subjecting the effluent from the lime precipitation step to carbon adsorption.

Ion exchange can be employed as an alternative to the lime precipitation process. While ion exchange has been reported to produce lower effluent concentrations (0.03 mg/l) than that achievable by lime precipitation, it usually entails much higher capital and operating costs. Ion exchange becomes more practical when the waste streams are relatively small and contain high concentrations of copper.

Lead

The most commonly employed process for the removal of soluble lead from waste water is precipitation under alkaline conditions followed by sedimentation and filtration.

Under alkaline conditions (usually created by the addition of lime) lead will precipitate out of solution and form solid particles of lead carbonate and lead hydroxide. As with the removal of copper, it is often necessary to also add coagulants to produce precipitates of sufficient size. Precipitation followed by sedimentation has been reported to produce effluent lead concentrations on the order of 0.5 mg/liter. If the sedimentation step is followed by filtration, an effluent lead concentration of 0.03 mg/liter may be achieved.

Ion exchange, while reported to produce lower lead concentrations, usually entails a much higher capital and operating cost than lime precipitation.

Mercury

The most promising and technically proven processes currently available for the removal of low concentrations of soluble mercury from large waste water streams are ion exchange or sulfide precipitation.

In the ion exchange process, the waste water, after sedimentation for the removal of any free mercury, is passed through a proprietary ion exchange resin. Mercury is removed as the mercuric chloride complex anion. A second stage ion exchange step serves as a polishing step and reduces the mercury concentration down to very low levels. Concentrations of less than 0.005 mg/liter have been reported.

In the sulfide precipitation process mercurous and organic mercury compounds must first be oxidized to the mercuric ion. Lime and sulfide are then added along with coagulant aids in order to promote the formation of mercuric sulfide precipitates. The precipitates are removed from the waste water stream by means of sedimentation and filtration, as in the copper and lead removal processes. This process has been reported to be capable of producing an effluent mercury concentration of 0.1 to 0.3 mg/liter.

In addition to ion exchange and sulfide precipitate several newly developed organic adsorbents and complexing agents have shown promising results in laboratory tests.

The entire technology for the removal of mercury has not been developed very far in terms of full scale actual plant operation.

Fluoride

Precipitation with lime is the standard technique for the reduction of high concentrations of soluble fluoride. The fluoride is precipitated as calcium fluoride. While the theoretical solubility limit for calcium fluoride is approximately 8 mg/liter at pH11, effluent concentrations of less than 20 mg/liter are seldom achieved due to the slow reaction rates, difficulty in separating colloidal particles of calcium fluoride, and the interference of other ions. The addition of alum and other coagulants encourages the formation of larger and more readily removable precipitates.

Where effluents fluoride concentrations lower the 20 mg/liter are required, various adsorptive techniques must be used.

In such processes the fluoride containing water is passed through contact beds of hydroxylapatite or activated alumina. Adsorptive on activated alumina has been reported to be capable of producing effluent fluoride concentrations as low as 1.0 mg/liter. The use of adsorptive techniques has largely been confined to the treatment of municipal drinking water containing undesirably high concentrations of fluoride.

Cyanide

The process most frequently employed for the treatment of waste water containing cyanide is destruction by chlorination under alkaline conditions. In this process the cyanide may be partially oxidized to cyanate or totally oxidized to carbon dioxide and nitrogen, depending on the chlorine dosage.

Theoretically, if sufficient chlorine is added and sufficient contact time provided, complete oxidation of cyanide should be achievable. In reality, the presence of small quantities of soluble iron often causes the formation of extremely stable ferrocyanide complexes which prevent the complete oxidation of cyanide.

In recent years ozonation has shown to be effective in oxidizing cyanides. There are indications that ozonation is more effective than alkaline chlorination in attacking the more difficult to oxidize metal complexes of cyanide.

Both the alkaline chlorination and ozonation processes can become prohibitively expensive if the cyanide containing waste water also contains large quantities of oxidizable organic material which will unavoidably be oxidized along with the cyanide.

Oil and Grease

Oil and grease are usually present in waste waters both in the suspended and emulsified form.

Particles of suspended oil and grease are generally removed by means of gravity separators. Such separators can typically remove 90-95 percent of the suspended oil, but are totally ineffective in removing emulsified oil.

To remove emulsified oil, the emulsion must first be broken by chemical means consisting of the addition of acids and/or coagulant salts such as alum. After so treated, the oil can be removed by flotation or filtration. The concentration of oil and grease in the treated effluent depends largely on the degree of success in breaking the emulsion. Generally an oil and grease concentration of less than 30 mg/liter should be achievable by emulsion breaking and gravity separation. If filtration is employed, a concentration of 10 mg/liter should be achievable.

Depending on conditions, varying amounts of emulsified oil may be removed along with other biodegradable material in standard biological treatment processes.

SECTION VIII

COST, ENERGY, AND NONWATER QUALITY ASPECTS

Approximately 160 company operations participate in the manufacture of the fifteen synthetic polymer products (see Table VIII-1). The actual number of plants is not known. Some of the 60 company operations include multi-plant divisions; many more are part of multiproduct plants.

Total production in the 1972-1973 time frame was estimated at 1.2 million kkg (2.6 billion lbs) per year or about one-tenth of the volume (26 billion lbs) represented by the larger-volume resins studies earlier. Together (i.e., these fifteen polymers and the earlier eighteen resins) the products covered in the two studies were estimated to represent 99 percent of the total production of synthetic and plastic materials.

Current discharge resulting from the production of synthetic polymers was estimated at 90 thousand cubic meters per day (24 MGD). Water discharges (at current hydraulic loads) was projected to increase at 10 per cent through 1977, while production was projected to increase at 14 percent in the same period. Approximately 25 percent of current discharge by the industry was estimated to be treated in municipal plants.

The first part of this section (Tables VIII-1 to VIII-4) summarizes the costs (necessarily generalized) of end-of-pipe treatment systems either currently in use or recommended for future use in synthetic polymers production facilities. Costs have been estimated for all fifteen product categories even though specific guidelines or standards were not recommended. Lacking specific effluent requirements, appropriate control technologies were assumed which were consistent with existing knowledge of waste composition.

In order to reflect the different treatment economics of existing versus new plants, large versus small plants, free-standing versus joint treatment facilities, or municipal versus industrial facilities, costs have been developed typically for more than one plant situation in each product subcategory. These productspecific analyses are presented in Tables VIII-4/1 to VIII-4/30.

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Cost Models of Treatment Technologies

Information on treatment cost experience was more scarce in the production of synthetic polymers than it was from the resin facilities studied earlier. In large part this was due to the small number of free-standing plants in this industry. There is also much greater dependence upon municipal treatment for these smaller-volume products than was true for resin production. More important, much of the wastes resulting from these products are treated in the central facilities of the large chemical complexes in which they are located. Many times the main production in these multi-product plants includes the resins covered earlier.

Consequently, the basic data for estimating the costs of treating the wastes from synthetic polymers was that developed in the first study. These cost models were developed around standard waste water treatment practice and compared to actual data from a dozen resin plants. That comparison resulted in deviations within ± 20 percent of model values. For details on the basis of the cost models and their assumptions, see the cost section of the development document for the resins industry segment (16).

Cost-Effectiveness Perspectives

Rough estimates were made of the existing degree of BOD_5 removal by either industrial or municipal systems in the fifteen product groups. A 74 percent weighted average removal of BOD_5 was calculated for these synthetic polymers in 1972. This is substantially higher than the 42 percent removal for resin products because of the higher use of municipal systems for polymer wastes and the availability of larger central industrial treatment systems to handle the lower volumes of these wastes. By 1977, the average removal implicit in BPCTCA requirements is estimated at 90 percent. This is lower than the 95 percent to be required of resin production because, again, of the larger proportion of municipal treatment - for which 85 percent removal is expected.

Annual Cost Perspectives

Annual costs for existing plants were roughly estimated at $1.8 million. The expected annual costs for existing synthetic polymers plants in 1977 consistent with best practicable technology was estimated at $5.0 million. This estimate (Table VIII-2) was the result of the following considerations: the production volumes and waste loads for each of the fifteen product groups; the average costs of treatment for different plant sizes; or the costs to be expected from handling these wastes as part of a larger municipal or industrial system. Similarly, by 1983, the estimated costs (Table VIII-2) for existing plants using best available technology were $12.0 million. It is noted that these costs were associated with endof-pipe treatment only. Costs for in-plant additions or modifications were not included.

The above annual cost estimates for existing plants for 1972, 1977, and 1983 indicate average increases of 23 percent per year between 1972 and 1977, and 20 percent per year between 1977 and 1983. Much of the estimated increase in costs between 1972 and 1977 was tied to the assumed full payment of charges for the use of municipal facilities. User charges for treatment services beyond secondary biological treatment in municipal systems were not considered appropriate before 1983. To the costs for existing plants must be added the costs associated with new plants, governed by BADT-NSPS. Assuming the production volume of new plants to be equal to the expected growth in production, the potential annual cost associated with new plants in 1977 was estimated at $3.4 million (Table VIII-2). Altogether, that means that the industry's annual costs are expected to increase 36 percent per year (from $1.8 million in 1972 to $8.3 million (5.0 + 3.3) in 1977), this supported by a sales growth of 14 percent per year. A similar estimate for 1983 has been precluded by the lack of a meaningful forecast of product growth.

Cost Per Unit Perspectives

Another measure by which to gauge the importance of the costs in Table VIII-2 is to relate them to the sales price of the products as is done in Table VIII-3. The average range of water pollution control costs under BPCTCA was estimated at 0.3 percent to 1.3 percent of current sales prices. On average, the range of costs for applying BATEA to existing plants was 0.6 to 3.3 percent of sales price. The cost of BADT-NSPS was estimated at 0.5 percent of sales price over the fifteen products. These cost impacts are lower on average than those for the eighteen resin products studied earlier primarily because the average price of these polymers is higher.

Waste Water Treatment Cost Estimates

The average range of water pollution control costs (Table VIII-4) under BPCTCA, BATEA, and BADT-NSPS technologies respectively were $0.16 ($0.63), $0.40 ($1.52), and $0.17 ($0.66) per cubic meter (per thousand gallons). Table VIII-4 and its 30 associated tables portray the costs of major treatment steps required to achieve the recommended technologies. Where municipal user charges are not considered directly, the appropriate charge would be $0.39 or $0.63 per thousand gallons depending on the size economies of the representative municipal system.

In each of the representative plant cost analyses, typical plant situations were identified in terms of production capacity, hydraulic load, and treatment plant size. Capital costs have been assumed to be a constant percentage (8 percent) of fixed investment. Depreciation costs have been calculated consistent with the faster write-off (financial life) allowed for these facilities (10 percent per year) over 10 years even though the physical life is longer.

Cost-effectiveness relationships are implicit in the calculation of these costs together with the effluent levels achieved by each treatment step in each major relevant pollutant dimension. These effluent levels are indicated at the bottom of each representative plant sheet.

Industrial Waste Treatment Model Data

In Tables VIII-5/1 to VIII-5/3 the total discharges for each product subcategory are estimated for 1972 and 1977. The quality of effluents remaining untreated in 1977 is indicated as that consistent with the application of BPCTCA technology. Finally, the current status of treatment in each product group is estimated in terms of the proportion utilizing primary treatment and that utilizing a form of biological treatment, whether industrial or municipal.

Energy Cost Perspectives

Each of the representative plant analyses in the 30 tables summarized by Table VIII-4 includes an estimate of energy costs (of control). The basis for these energy cost estimates was explained in the earlier development document for resins production. The most important assumption therein was one of 1972 energy prices. That assumption has been retained, for purposes of comparison, in this analysis of polymers production.

Generally, the biological treatment systems employed by industries and municipalities are not large consumers of energy. By the cost models employed in this report, the energy costs of BPCTCA and BADT-NSPS technologies in this industry were estimated at about 2 percent of the total annual waste water treatment costs in Table VIII-2. The add-on technologies for BATEA compliance, however, were estimated to raise that proportion to 7 percent by 1983.

Non Water Quality Effects

The nonwater quality aspects of the treatment and control technology found in the synthetics and plastics industry are related to (1) the disposal of solids or slurries resulting from waste water treatment and in-process plant control methods, (2) the generation of a by-product of commercial value, (3) disposal of off-specification and scrap products, and (4) the creation of problems of air pollution and land utilization. These effects were discussed in the development document for resins production.

Other nonwater quality aspects of treatment and pollution control are minimal in this industry and largely depend upon the type of waste water treatment technology employed. In general, noise levels from typical waste water treatment plants are not excessive. If incineration of waste sludges is employed, there is potential for air pollution, principally particulates and possibly nitrogen oxides, although the latter should be minimal because incineration of sludges does not normally take place at temperature levels where the greatest amounts of nitrogen oxide are generated. There are no radioactive nuclides used within the industry, other than in instrumentation, so that no radiation problems will be encountered. Odors from the waste water treatment plants may cause occasional problems since waste waters are sometimes such that heavy, stable, foams occur on aerated basins and septicity is present. But, in general, odors are not expected to be a significant problem when compared with odor emissions possible from other plant sources.

The final part of this section reports on updated inputs for EPA's Industrial Waste Treatment Model (Tables VIII-5/1 to VIII-5/3). The estimated total volume of waste waters discharged for product subcategories has been estimated for 1972-1977. Also, general estimates of the current level and source of treatment in different industry segments have been made.

Alternative Treatment Technologies

The range of components used or needed to effect best practicable control technology currently available (BPCTCA), best available technology economically achievable (BATEA), and best available demonstrated technology for new source performance standards (BADT-NSPS) in this portion of the plastics and synthetics industry have been combined into eight alternative end-of-pipe treatment steps. These are as follows:

A. Initial Treatment: For removal of suspended solids and heavy metals. Includes equalization, neutralization, chemical coagulation or precipitation, API separators, and primary clarification.

B. Biological Treatment: Primarily for removal of BOD. Includes activated sludge (or aerated stabilization basins), sludge disposal, and final clarification.

C. Multi-Stage Biological: For further removal of BOD loadings. Either another biological treatment system in series or a long-residence-time polishing lagoon.

D. Granular Media Filtration: For further removal of suspended solids (and heavy metals) from biological treatment effluents. Includes some chemical coagulation as well as granular media filtration.

E. Physical-Chemical Treatment: For further removal of COD, primarily that attributable to refractory organics, e.g., with activated carbon adsorption.

F. Liquid Waste Incineration: For complete treatment of small volume wastes.

G. Municipal Treatment: Conventional municipal treatment of industrial discharge into sewer collection systems. Primary settling and secondary biological stages assumed.

TABLE VIII-1

PERSPECTIVES ON THE PRODUCTION OF SYNTHETIC POLYMERS WATER USAGE

Guidelines Subcategory Product	Number of Company Operations(1)	Percent of Total 15 Product Production(2)	Percent of Water Used by 15 Products	Percent of Growth In Water Usage of 15 Products: 1972-1977
I				
EVA Copolymers	5	5.9	0.8	0.7
Fluorocarbons	5	1.0	4.6	2.6
Polypropylene Fibers	3	5.5	1.7	1.3
Polyvinylidene Chloride	4	1.0	0.4	0
II				
Acrylic Resins	>4	11.8	14.6	34.4
Cellulose Derivatives	3	3.9	17.6	8.6
Subtotal - A&B	>24	29.1	39.7	47.6
III				
Alkyd and Unsaturated Polyester Resins	>14	58.8	7.5	11.9
Cellulose Nitrate	2	2.0	10.9	0
Polyamids	3	1.0	0.8	0.6
Polyesters (thermoplastic)	3	0.2	0.4	0.6
Polyvinyl Butyral	2	1.6	5.9	2.6
Polyvinyl Ethers	2	0.4	0.4	0.6
Silicones	4	5.1	33.2	32.9
IV				
Nitrile Barrier Resins	3	1.0	0.8	3.2
Spandex Fibers	3	0.8	0.4	0
Subtotal - C&D	>36	70.9	60.3	52.4
Total - 15 Products	>60	100.0	100.0	100.0

(1) Number of companies producing each of the products; the number of plants is greater because of multiple sites for any one company.

(2) Estimated annual 15-product production in 1972-73 period: 1.15B kkg (2.55 B lbs).

(3) Result of projected product growth at current representative hydraulic loads.

TABLE VIII-2

PERSPECTIVES ON SYNTHETIC POLYMERS PRODUCTION ANNUAL TREATMENT COSTS

Guidelines Subcategory Product	Total Annual Costs, $MM		
	Existing Plants		New Plants
	1977	1983	1983
I			
EVA Copolymers	0.12	0.37	0.10
Fluorocarbons	0.36	0.36	0.13
Polypropylene Fibers	0.17	0.17	0.08
Polyvinylidene Chloride	0.01	0.04	0.00
II			
Acrylic Resins	0.58	0.64	0.86
Cellulose Derivatives	0.97	2.84	0.34
III			
Alkyds and Unsaturated Polyester Resins	0.45	0.59	0.45
Cellulose Nitrate	0.30	0.31	0.00
Polyamides	0.08	0.22	0.04
Polyesters (thermoplastic)	0.03	0.07	0.03
Polyvinyl Butyral	0.30	0.92	0.09
Polyvinyl Ethers	0.03	0.07	0.03
Silicones	1.56	5.21	1.13
IV			
Nitrile Barrier Resins	0.04	0.08	0.12
Spandex Fibers	0.04	0.08	0.00
Total	5.04	12.17	3.40

TABLE VIII-3

PERSPECTIVES ON SYNTHETIC POLYMERS PRODUCTION COST IMPACT

Guideline Subcategory Product	Price Level ¢/lb	Control Cost Range as % of Sales Price		
		BPCTCA %	BATEA %	BADT %
I				
EVA Copolymers	15	1.0 - 2.0	2.3 - 6.2	1.0
Fluorocarbons	325	0.1 - 0.6	0.1 - 0.6	0.1
Polypropylene Fibers	35	0.7 - 1.4	0.7 - 1.4	0.7
Polyvinylidene Chloride	55	0.1 - 0.2	0.1 - 0.7	0.1
II				
Acrylic Resins	70	0.1 - 0.4	0.1 - 0.4	0.1
Cellulose Derivatives	50	1.1 - 2.0	3.3 - 5.7	1.2
III				
Alkyd and Unsaturated Polyester Resins	20	0.4 - 1.9	0.4 - 3.8	0.8
Cellulose Nitrate	50	0.8 - 1.7	1.0 - 3.6	0.9
Polyamide	130	0.1 - 0.9	0.2 - 2.5	0.2
Polyesters (thermoplastic)	70	0.1 - 2.9	0.3 - 6.4	0.2
Polyvinyl Butyral	70	0.4 - 2.1	0.4 - 10.7	0.8
Polyvinyl Ethers	100	0.2 - 0.7	0.2 - 1.8	0.3
Silicones	100	0.6 - 1.2	1.7 - 3.5	0.7
IV				
Nitrile Barrier Resins	60	0.1 - 0.6	0.1 - 1.3	0.3
Spandex Fibers	100	0.1 - 0.3	0.1 - 0.5	0.2
Unweighted Average		0.4 - 1.3	0.7 - 3.3	0.5

TABLE VIII-4

SUMMARY OF WATER EFFLUENT TREATMENT COSTS[1]
COST PER UNIT VOLUME BASIS

Guidelines Subcategory Product	BPCTCA COSTS		BATEA COSTS		BADT COSTS[2]	
	$/cu m	$/1000 gal	$/cu m	$/1000 gal	$/cu m	$/1000 gal
I						
EVA Copolymers	0.16	0.60	0.49	1.85	0.16	0.60
Fluorocarbons	0.26	1.00	0.26	1.00	0.26	1.00
Polypropylene Fibers	0.33	1.25	0.33	1.25	0.33	1.25
Polyvinylidene Chloride	0.9 - 0.13	0.35 - 0.50	0.13 - 0.53	0.50 - 2.00	0.12	0.45
II						
Acrylic Resins	0.13	0.50	0.15	0.55	0.13	0.50
Cellulose Derivatives	0.18	0.70	0.54	2.05	0.21	0.80
III						
Alkyd and Unsaturated Polyester Resins	0.13 - 0.66	0.50 - 2.50	0.13 - 1.32	0.50 - 5.00	0.20	0.75
Cellulose Nitrate	0.08 - 0.11	0.30 - 0.40	0.11 - 0.22	0.40 - 0.85	0.11	0.40
Polyamids	0.32	1.20	0.87	3.30	0.32	1.20
Polyesters (thermoplastic)	0.26	1.00	0.59	2.25	0.26	1.00
Polyvinyl Butyral	0.13 - 0.26	0.50 - 100	0.13 - 1.32	0.50 - 5.00	0.18	0.70
Polyvinyl Ethers	0.13 - 0.26	0.50 - 1.00	0.13 - 0.66	0.50 - 2.50	0.24	0.90
Silicones	0.09 - 0.22	0.35 - 0.85	0.26 - 0.66	1.00 - 2.50	0.18	0.70
IV						
Nitrile Barrier Resins	0.13 - 0.18	0.50 - 0.70	0.13 - 0.40	0.50 - 1.50	0.18	0.70
Spandex Fibers	0.13 - 0.33	0.50 - 1.25	0.13 - 0.66	0.50 - 2.50	0.33	1.25
Average	0.17	0.63	0.40	1.52	0.17	0.66

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[1] Assume 330 day /year operation. Estimated proportions treated municipal systems factored in at $0.50/1000 gal.

[2] Assume new plants are larger facilities with minimum flows. New plant production assumed equivalent to growth between 1972 and 1977.

TABLE VIII-4/1

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory: Ethylene Vinyl Acetate

Plant Description: Small Plant - Large Industrial Complex

Representative Plant Capacity million kilograms (pounds) per year:	11.3	(25)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	11.9	(1.3)
Treatment Plant Size thousand cubic meters per day (MGD):	6.4	(1.7)*

Costs - $1000	Alternative Treatment Steps			
	A	B	D	E
Initial Investment	28	65	15	106
Annual Costs:				
Capital Costs (8%)	2.2	5.2	1.2	8.5
Depreciation (10%)	2.8	6.5	1.5	10.6
Operation and Maintenance	0.3	3	0.3	15.9
Energy and Power	0.1	0.3	-	4
Total Annual Costs	5.4	15	3	39

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)			
		A	B	D	E
B.O.D.	1	-	0.1	-	0.08
C.O.D.	2	-	1	-	0.7
Suspended Solids	N/A	0.3	-	0.05	-

*The EVA contribution is 0.4 thousand cubic meters per day (0.1 mgd). This is approximately 6% of the total flow to be treated.

TABLE VIII-4/2

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory: Ethylene Vinyl Acetate

Plant Description: Large Plant - Industrial Complex

Representative Plant Capacity million kilograms (pounds) per year:	22.7	(50)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	11.9	(1.3)
Treatment Plant Size thousand cubic meters per day (MGD):	6.8	(1.8)*

Costs - $1000	Alternative Treatment Steps			
	A	B	D	E
Initial Investment	53	124	29	204
Annual Costs:				
Capital Costs (8%)	4.1	9.8	2.3	16
Depreciation (10%)	5.3	12.4	2.9	20
Operation and Maintenance	0.5	5.3	0.4	32
Energy and Power	0.1	0.5	-	8
Total Annual Costs	10	28	5.6	77

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)			
		A	B	D	E
B.O.D.	1	-	0.1	-	0.08
C.O.D.	2	-	1	-	0.7
Suspended Solids	N/A	0.3	-	0.05	-

* The EVA contribution is 0.8 thousand cubic meters per day (0.2 mgd). This is approximately 11% of the total flow to be treated.

TABLE VIII-4/3

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory: Fluorocarbons

Plant Description: Small Plant - Free Standing

Representative Plant Capacity million kilograms (pounds) per year:	1.4	(3)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	125	(15.0)
Treatment Plant Size thousand cubic meters per day (MGD):	0.5	(0.14)

Costs - $1000	Alternative Treatment Steps A
Initial Investment	44
Annual Costs:	
Capital Costs (8%)	3.5
Depreciation (10%)	4.4
Operation and Maintenance	2.0
Energy and Power	0.1
Total Annual Costs	10

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product) A
B.O.D.	3	2
C.O.D.	20	20
Suspended Solids	5	5

TABLE VIII-4/4

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory:	Fluorocarbons	
Plant Description:	Small Plant - Municipal Discharge	
Representative Plant Capacity million kilograms (pounds) per year:	1.4	(3)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	125	(15.0)
Treatment Plant Size thousand cubic meters per day (MGD):	0.5	(0.14)

Costs - $1000	Alternative Treatment Steps P*	 M_1	 M_2
Initial Investment	102	-	-
Annual Costs:			
Capital Costs (8%)	8	-	-
Depreciation (10%)	10	-	-
Operation and Maintenance	4	-	-
Energy and Power	1	-	-
Total Annual Costs	23	18	29

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)
B.O.D.	3	
C.O.D.	20	(municipal treatment)
Suspended Solids	5	

* Neutralization of acids

M_1 is the municipal treatment charge associated with a 38 to 76 thousand cubic meters per day (10-20 mgd) treatment plant. A charge of 39¢ per 1000 gallons has been used.

M_2 is associated with a 4 to 12 thousand cubic meters per day (1-3 mgd) municipal plant. A charge of 63¢ per 1000 gallons has been used.

TABLE VIII-4/5

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory: Fluorocarbons

Plant Description: Large Plant - Free Standing

Representative Plant Capacity million kilograms (pounds) per year:	6.8	(15)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	125	(15.0)
Treatment Plant Size thousand cubic meters per day (MGD):	2.6	(0.7)

Costs - $1000	Alternative Treatment Steps A
Initial Investment	145
Annual Costs:	
Capital Costs (8%)	11.6
Depreciation (10%)	14.5
Operation and Maintenance	8.6
Energy and Power	0.3
Total Annual Costs	35

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product) A
B.O.D.	3	2
C.O.D.	20	20
Suspended Solids	5	5

TABLE VIII-4/6

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory: Fluorocarbons

Plant Description: Large Plant - Municipal Discharge

Representative Plant Capacity million kilograms (pounds) per year:	6.8	(15)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	125	(15.0)
Treatment Plant Size thousand cubic meters per day (MGD):	2.6	(0.7)

Costs - $1000	Alternative Treatment Steps		
	P*	M_1	M_2
Initial Investment	285	-	-
Annual Costs:			
Capital Costs (8%)	23	-	-
Depreciation (10%)	29	-	-
Operation and Maintenance	6	-	-
Energy and Power	1	-	-
Total Annual Costs	59	88	142

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)
B.O.D.	3	(Municipal treatment)
C.O.D.	20	
Suspended Solids	5	

* Neutralization of Acids

TABLE VIII-4/7

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory:	Polypropylene Fibers	
Plant Description:	Free Standing Treatment Plant	
Representative Plant Capacity million kilograms (pounds) per year:	20.4	(45)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	8.3	(1.0)
Treatment Plant Size thousand cubic meters per day (MGD):	0.5	(0.14)

Costs - $1000	Alternative Treatment Steps		
	A	D	E
Initial Investment	96	50	433
Annual Costs:			
Capital Costs (8%)	8	4	35
Depreciation (10%)	10	5	43
Operation and Maintenance	2	2	115
Energy and Power	0.5	-	10
Total Annual Costs	20.5	11	203

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)		
		A	D	E
B.O.D.	0.5	0.3	-	0.1
C.O.D.	1.5	1.3	-	0.2
Suspended Solids	1.0	0.5	0.1	-

TABLE VIII-4/8

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory: Polypropylene Fibers

Plant Description: Municipal Discharge

Representative Plant Capacity million kilograms (pounds) per year:	20.4	(45)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	8.3	(1.0)
Treatment Plant Size thousand cubic meters per day (MGD):	0.5	(0.14)

Costs - $1000	Alternative Treatment Steps		
	P*	M_1	M_2
Initial Investment	89	-	-
Annual Costs:			
Capital Costs (8%)	7	-	-
Depreciation (10%)	9	-	-
Operation and Maintenance	18	-	-
Energy and Power	1	-	-
Total Annual Costs	35	18	29

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)
B.O.D.	0.5	
C.O.D.	1.5	(Municipal Treatment)
Suspended Solids	1.0	

*Air flotation for oil and grease removal.

TABLE VIII-4/9

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory:	Polyvinylidene Chloride	
Plant Description:	Small Plant - Industrial Complex	
Representative Plant Capacity million kilograms (pounds) per year:	2.3	(5)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	4.2	(0.5)
Treatment Plant Size thousand cubic meters per day (MGD):	1.7	(0.45)*

Costs - $1000

	Alternative Treatment Steps		
	A	D	E
Initial Investment	4	2	11
Annual Costs:			
Capital Costs (8%)	0.3	0.2	0.9
Depreciation (10%)	0.4	0.2	1.1
Operation and Maintenance	0.06	0.1	1.8
Energy and Power	0.04	-	0.2
Total Annual Costs	0.8	0.5	4.0

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)
B.O.D.	0	(No specific guidelines)
C.O.D.	8	
Suspended Solids	0.2	

*The PVCl contribution is 0.03 thousand cubic meters per day (0.007 MGD); this is approximately 1.5% of the total flow to be treated.

TABLE VIII-4/10

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory:	Polyvinylidene Chloride	
Plant Description:	Large Plant - Industrial Complex	
Representative Plant Capacity million kilograms (pounds) per year:	11.3	(25)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	4.2	(0.5)
Treatment Plant Size thousand cubic meters per day (MGD):	1.7	(0.45)*

Costs - $1000	Alternative Treatment Steps		
	A	D	E
Initial Investment	21	11	55
Annual Costs:			
Capital Costs (8%)	1.7	9	4.4
Depreciation (10%)	2.1	11	5.5
Operation and Maintenance	0.2	0.1	9.4
Energy and Power	0.1	-	1.5
Total Annual Costs	4	20.1	21

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)
B.O.D.	0	(No specific guidelines)
C.O.D.	8	
Suspended Solids	0.2	

*The PVCl contribution is 0.13 thousand cubic meters per day (0.035 MGD); this is approximately 20% of the total flow to be treated.

TABLE VIII-4/11

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory: Acrylic Resins

Plant Description: Small Plant - Industrial Complex

Representative Plant Capacity
million kilograms (pounds) per year: 9.1 (20)

Hydraulic Load
cubic meters/metric ton of product:
(gal/lb) 32 (3.8)

Treatment Plant Size
thousand cubic meters per day (MGD): 17.4 (4.6)*

Costs - $1000	Alternative Treatment Steps		
	A	B	D
Initial Investment	45	110	24
Annual Costs:			
Capital Costs (8%)	4	9	1.9
Depreciation (10%)	5	11	2.4
Operation and Maintenance	0.4	6.5	0.2
Energy and Power	0.1	0.5	-
Total Annual Costs	9.5	27	4.5

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)
B.O.D.	15	(No specific guidelines)
C.O.D.	30	
Suspended Solids	7.5	

*The acrylic resin contribution is 0.9 thousand cubic meters per day (0.23 MGD), this is approximately 5% of the total flow to be treated.

TABLE VIII-4/12

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory:	Acrylic Resins	
Plant Description:	Large Plant - Industrial Complex	
Representative Plant Capacity million kilograms (pounds) per year:	54.4	(120)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	32	(3.8)
Treatment Plant Size thousand cubic meters per day (MGD):	13.1	(3.46)*

Costs - $1000	Alternative Treatment Steps A	B	D
Initial Investment	296	724	156
Annual Costs:			
Capital Costs (8%)	24	58	12
Depreciation (10%)	30	72	16
Operation and Maintenance	3	36	1
Energy and Power	1	3	-
Total Annual Costs	58	169	29

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)
B.O.D.	15	
C.O.D.	30	(No specific guidelines)
Suspended Solids	7.5	

*The acrylic resin contribution is 5.2 thousand cubic meters per day (1.38 MGD), this is approximately 40% of the total flow to be treated.

TABLE VIII-4/13

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory:	Cellulose Derivates	
Plant Description:	Small Plant - Industrial Complex	
Representative Plant Capacity million kilograms (pounds) per year:	4.5	(10)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	117	(14)
Treatment Plant Size thousand cubic meters per day (MGD):	8	(2.1)*

Costs - $1000	Alternative Treatment Steps A	B	D	E
Initial Investment	104	256	56	334
Annual Costs:				
Capital Costs (8%)	8	20	4.5	27
Depreciation (10%)	10	26	5.6	33
Operation and Maintenance	3	18	0.6	33
Energy and Power	0.5	8	-	8
Total Annual Costs	21.5	72	10.7	101

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)
B.O.D.	180	(No specific guidelines)
C.O.D.	650	
Suspended Solids	20	

*The cellulose derivative contribution is 1.6 thousand cubic meters per day (0.42 MGD); this is approximately 20% of the total flow to be treated.

TABLE VIII-4/14

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory: Cellulose Derivatives

Plant Description: Large Plant - Industrial Complex

Representative Plant Capacity million kilograms (pounds) per year:	22.7	(50)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	117	(14)
Treatment Plant Size thousand cubic meters per day (MGD):	151	(40)*

Costs - $1000	Alternative Treatment Steps			
	A	B	D	E
Initial Investment	154	376	220	636
Annual Costs:				
Capital Costs (8%)	12	30	18	51
Depreciation (10%)	15	38	22	64
Operation and Maintenance	5	54	4	200
Energy and Power	2	38	-	50
Total Annual Costs	34	160	44	365

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)
B.O.D.	180	(No specific guidelines)
C.O.D.	650	
Suspended Solids	20	

*The cellulose derivatives contribution is 8.0 thousand cubic meters per day (2.12 MGD); this is approximately 5% of the total flow to be treated.

TABLE VIII-4/15

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory:	Alkyds and Unsaturated Polyester Resins	
Plant Description:	Large Plant - Once-thru Scrubber - Free Standing	
Representative Plant Capacity million kilograms (pounds) per year:	15.9	(35)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	3.3	(0.4)
Treatment Plant Size thousand cubic meters per day (MGD):	0.15	(0.04)

Costs - $1000	Alternative Treatment Steps		
	A	B*	C**
Initial Investment	30	84	84
Annual Costs:			
Capital Costs (8%)	2.4	6.7	6.7
Depreciation (10%)	3.0	8.4	8.4
Operation and Maintenance	2.4	15.3	10.4
Energy and Power	0.2	0.6	0.5
Total Annual Costs	8	31	26

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)		
		A	B	C
B.O.D.	10	-	0.2	0.07
C.O.D.	25	-	1	0.3
Suspended Solids	1	0.1	-	0.02

*Two-stage biological treatment
**Two additional stages of biological treatment

TABLE VIII-4/16

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory: Alkyds and Unsaturated Polyester Resins

Plant Description: Small Plant - Recirculating Scrubber - Municipal Discharge

Representative Plant Capacity million kilograms (pounds) per year:	2.3	(5)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	0.4	(0.05)
Treatment Plant Size thousand cubic meters per day (MGD):	0.003	(0.001)

Costs - $1000	Alternative Treatment Steps		
	P*	M_1	M_2
Initial Investment	5.0	-	-
Annual Costs:			
Capital Costs (8%)	0.4	-	-
Depreciation (10%)	0.5	-	-
Operation and Maintenance	1.0	-	-
Energy and Power	-	-	-
Total Annual Costs	1.9	0.1	0.2

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)
B.O.D.	10	
C.O.D.	25	(Municipal Treatment)
Suspended Solids	1	

*Pretreatment is Clarification or Filtration.

TABLE VIII-4/17

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory: Alkyds and Unsaturated Polyester Resins

Plant Description: Large Plant - Recirculating Scrubber-Free Standing

Representative Plant Capacity million kilograms (pounds) per year:	15.9	(35)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	0.4	(0.05)
Treatment Plant Size thousand cubic meters per day (MGD):	0.15	(0.04)*

Costs - $1000	Alternative Treatment Steps		
	A	B**	C***
Initial Investment	30	84	84
Annual Costs:			
Capital Costs (8%)	2.4	6.7	6.7
Depreciation (10%)	3.0	8.4	8.4
Operation and Maintenance	2.4	15.3	10.4
Energy and Power	0.2	0.6	0.5
Total Annual Costs	8	31	26

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)		
		A	B	C
B.O.D.	10	-	0.2	0.07
C.O.D.	25	-	1	0.3
Suspended Solids	1	0.1	-	0.02

*Dilution of 7:1 for effective operation of the biological treatment has been allowed.

**Two-stage biological treatment.

***Two additional stages of biological treatment.

TABLE VIII-4/18

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory:	Alkyds and Unsaturated Polyester Resins	
Plant Description:	Large Plant - Recirculating Scrubber - Municipal Discharge	
Representative Plant Capacity million kilograms (pounds) per year:	15.9	(35)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	0.4	(0.05)
Treatment Plant Size thousand cubic meters per day (MGD):	0.02	(0.005)

Costs - $1000 — **Alternative Treatment Steps**

	P*	M_1	M_2
Initial Investment	10	-	-
Annual Costs:			
Capital Costs (8%)	0.8	-	-
Depreciation (10%)	1.0	-	-
Operation and Maintenance	1.0	-	-
Energy and Power	-	-	-
Total Annual Costs	2.8	0.7	1.1

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)
B.O.D.	10	
C.O.D.	25	(Municipal Treatment)
Suspended Solids	1	

*Pretreatment is clarification or filtration.

TABLE VIII-4/19

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory: Cellulose Nitrate

Plant Description: Plant in Industrial Complex

Representative Plant Capacity
million kilograms (pounds) per year: 18.1 (40)

Hydraulic Load
cubic meters/metric ton of product:
(gal/lb) 167 (20.0)

Treatment Plant Size
thousand cubic meters per day (MGD): 43.1 (11.4)*

Costs - $1000	Alternative Treatment Steps			
	A	B	D	E
Initial Investment	334	779	179	968
Annual Costs:				
Capital Costs (8%)	27	62	14	77
Depreciation (10%)	33	78	18	97
Operation and Maintenance	6.4	43	2	79
Energy and Power	0.6	9	-	22
Total Annual Costs	67	192	34	275

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)			
		A	B	D	E
B.O.D.	35	-	7	-	2
C.O.D.	75	-	23	-	14
Suspended Solids	85	4	-	1	-

*The cellulose nitrate contribution is 9.2 thousand cubic meters per day (2.43 MGD); this is approximately 20% of the total flow to be treated.

TABLE VIII-4/20

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory: Cellulose Nitrate

Plant Description: Plant with Municipal Discharge

Representative Plant Capacity million kilograms (pounds) per year:	18.1	(40)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	167	(20.0)
Treatment Plant Size thousand cubic meters per day (MGD):	9.1	(2.4)

Costs - $1000	Alternative Treatment Steps	
	P	M_1
Initial Investment	260	-
Annual Costs:		
Capital Costs (8%)	21	-
Depreciation (10%)	26	-
Operation and Maintenance	5.5	-
Energy and Power	0.5	
Total Annual Costs	53	309

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)
B.O.D.	35	
C.O.D.	75	(Municipal Treatment)
Suspended Solids	35	

TABLE VIII-4/21

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory:	Polyamides (Nylon 6/12)	
Plant Description:	Production in a Complex	
Representative Plant Capacity million kilograms (pounds) per year:	4.5	(10)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	16.7	(2.0)
Treatment Plant Size thousand cubic meters per day (MGD):	4.8	(1.26)*

Costs - $1000	Alternative Treatment Steps				
	A	B	C	D	E
Initial Investment	18	42	42	10	60
Annual Costs:					
Capital Costs (8%)	1.4	3.4	3.4	0.8	4.8
Depreciation (10%)	1.8	4.2	4.2	1.0	6.0
Operation and Maintenance	0.4	3.7	3.7	0.2	7.1
Energy and Power	0.1	1.7	1.7	-	1.1
Total Annual Costs	3.7	13	13	2	19

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)				
		A	B	C	D	E
B.O.D.	N/A	-	-	0.3	-	0.1
C.O.D.	N/A	-	-	3	-	1.2
Suspended Solids	N/A	0.2	-	-	0.07	-

*The polyamide contribution is 0.23 thousand cubic meters per day (0.06 MGD), this is approximately 5% of the total flow to be treated.

TABLE VIII-4/22

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUST

Industry Subcategory: Thermoplastic Polyester Resins

Plant Description: Large Plant - Industrial Complex

Representative Plant Capacity million kilograms (pounds) per year:	2.3	(5)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	8.3	(1.0)
Treatment Plant Size thousand cubic meters per day (MGD):	2.2	(0.58)*

Costs - $1000	Alternative Treatment Steps				
	A	B	C	D	E
Initial Investment	8	21	20	4	24
Annual Costs:					
Capital Costs (8%)	0.7	1.7	1.6	0.3	1.9
Depreciation (10%)	0.8	2.1	2.0	0.4	2.4
Operation and Maintenance	0.1	2.0	1.2	0.1	3.4
Energy and Power	0.03	0.2	0.2	-	0.3
Total Annual Costs	1.6	6	5	0.8	8

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)				
		A	B	C	D	E
B.O.D.	5	-	-	0.4	-	0.2
C.O.D.	15	-	-	5	-	1
Suspended Solids	N/A	0.2	-	-	0.08	-

*The thermoplastic resin contribution is 0.06 thousand cubic meters per day (0.015 MGD); this is approximately 3% of the total flow to be treated.

TABLE VIII-4/23

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory: Polyvinyl Butyral

Plant Description: Free Standing Treatment Plant

Representative Plant Capacity million kilograms (pounds) per year:	9.1	(20)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	96	(11.5)
Treatment Plant Size thousand cubic meters per day (MGD):	2.6	(0.7)

Costs - $1000	Alternative Treatment Steps			
	A	B	D	E
Initial Investment	285	725	135	1614
Annual Costs:				
Capital Costs (8%)	23	58	11	129
Depreciation (10%)	29	73	14	161
Operation and Maintenance	3	50	2	525
Energy and Power	0.5	4	-	155
Total Annual Costs	55.5	185	27	970

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)			
		A	B	D	E
B.O.D.	30	-	0.9	-	-
C.O.D.	40	-	9	-	-
Suspended Solids	N/A	-	-	0.5	-

TABLE VIII-4/24

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory:	Polyvinyl Ether	
Plant Description:	Plant in Industrial Complex	
Representative Plant Capacity million kilograms (pounds) per year:	1.8	(4)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	12.5	(1.5)
Treatment Plant Size thousand cubic meters per day (MGD):	2.3	(0.6)*

Costs - $1000	Alternative Treatment Steps			
	A	B	D	E
Initial Investment	8	21	4	25
Annual Costs:				
Capital Costs (8%)	0.6	1.7	0.3	2.0
Depreciation (10%)	0.8	2.1	0.4	2.5
Operation and Maintenance	0.1	1.1	0.1	4.0
Energy and Power	-	0.1	-	0.5
Total Annual Costs	1.5	5	0.8	9

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)
B.O.D.	N/A	
C.O.D.	25	(No specific guidelines)
Suspended Solids	N/A	

*The polyvinyl ether contribution is 0.07 thousand cubic meters per day (0.018 MGD); this is approximately 3% of the total flow to be treated.

TABLE VIII-4/25

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory:	Silicones	
Plant Description:	Fluids Only - Free Standing	
Representative Plant Capacity million kilograms (pounds) per year:	22.7	(50)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	54	(6.5)
Treatment Plant Size thousand cubic meters per day (MGD):	3.8	(1.0)

Costs - $1000

	Alternative Treatment Steps			
	A	B	D	E
Initial Investment	305	745	232	1338
Annual Costs:				
Capital Costs (8%)	24	60	19	107
Depreciation (10%)	31	75	23	134
Operation and Maintenance	6	40	2	228
Energy and Power	0.6	9	-	53
Total Annual Costs	61.6	184	44	522

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)			
		A	B	D	E
B.O.D.	N/A	-	1.5	-	0.6
C.O.D.	15	-	7.5	-	4.0
Suspended Solids	N/A	1.0	-	0.2	-

TABLE VIII-4/26

WATER EFFLUENT TREATMENT COSTS

PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory: Silicones

Plant Description: Fluids Only - Industrial Complex

Representative Plant Capacity million kilograms (pounds) per year:	22.7	(50)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	54	(6.5)
Treatment Plant Size thousand cubic meters per day (MGD):	43.5	(11.5)*

Costs - $1000	Alternative Treatment Steps			
	A	B	D	E
Initial Investment	143	334	77	436
Annual Costs:				
Capital Costs (8%)	11	27	6	35
Depreciation (10%)	14	33	8	44
Operation and Maintenance	3	18	1	36
Energy and Power	0.3	4	-	10
Total Annual Costs	28.3	82	15	125

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)			
		A	B	D	E
B.O.D.	N/A	-	1.5	-	0.6
C.O.D.	15	-	7.5	-	4.0
Suspended Solids	N/A	1.0	-	0.2	-

*The silicone contribution is 3.8 thousand cubic meters per day (1.0 MGD); this is approximately 9% of the total flow to be treated.

TABLE VIII-4/27

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory: Silicones
Multi-product - Free Standing

Plant Description:

Representative Plant Capacity million kilograms (pounds) per year:	22.7	(50)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	142	(17.0)
Treatment Plant Size thousand cubic meters per day (MGD):	17.2	(4.55)

Costs - $1000	Alternative Treatment Steps			
	A	B	D	E
Initial Investment	720	1760	441	3044
Annual Costs:				
Capital Costs (8%)	58	141	35	244
Depreciation (10%)	72	176	44	304
Operation and Maintenance	15	74	4	646
Energy and Power	2	14	-	200
Total Annual Costs	147	405	83	1394

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)			
		A	B	D	E
B.O.D.	85	-	7	-	3
C.O.D.	115	-	35	-	18
Suspended Solids	50	5	-	1	-

TABLE VIII-4/28

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory:	Silicones	
Plant Description:	Multi-product - Industrial Complex	
Representative Plant Capacity million kilograms (pounds) per year:	22.7	(50)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	142	(17.0)
Treatment Plant Size thousand cubic meters per day (MGD):	42.8	(11.3)*

Costs - $1000

	Alternative Treatment Steps			
	A	B	D	E
Initial Investment	509	1187	289	2191
Annual Costs:				
Capital Costs (8%)	41	95	23	175
Depreciation (10%)	51	119	29	219
Operation and Maintenance	9	66	2	622
Energy and Power	1	13		194
Total Annual Costs	102	293	54	1210

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)			
		A	B	D	E
B.O.D.	85	-	7	-	3
C.O.D.	115	-	35	-	15
Suspended Solids	50	5	-	1	-

*The silicone contribution is thousand cubic meters per day this is approximately 20% of the total flow to be treated.

TABLE VIII-4/29

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory: Nitrile Barrier Resins

Plant Description: Plant in Industrial Complex

Representative Plant Capacity million kilograms (pounds) per year:	4.5	(10)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	25	(3.0)
Treatment Plant Size thousand cubic meters per day (MGD):	8.3	(2.2)*

Costs - $1000	Alternative Treatment Steps A	B	D	E
Initial Investment	23	59	12	67
Annual Costs:				
Capital Costs (8%)	2	5	1	5
Depreciation (10%)	2	6	1	7
Operation and Maintenance	0.3	5	0.1	6
Energy and Power	0.1	1	-	1
Total Annual Costs	4.4	17	2.1	19

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)
B.O.D.	10	
C.O.D.	30	(No specific guidelines)
Suspended Solids	5	

*The nitrile barrier resin contribution is 0.34 thousand cubic meters per day (0.09 MGD); this is approximately 40% of the total flow to be treated.

TABLE VIII-4/30

WATER EFFLUENT TREATMENT COSTS
PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory:	Spandex Fibers	
Plant Description:	Plant in Industrial Complex	
Representative Plant Capacity million kilograms (pounds) per year:	2.3	(5)
Hydraulic Load cubic meters/metric ton of product: (gal/lb)	8.3	(1.0)
Treatment Plant Size thousand cubic meters per day (MGD):	3.4	(0.9)*

Costs - $1000	Alternative Treatment Steps			
	A	B	D	E
Initial Investment	8	16	3	21
Annual Costs:				
Capital Costs (8%)	0.6	1.3	0.2	1.7
Depreciation (10%)	0.8	1.6	0.3	2.1
Operation and Maintenance	0.2	1.4	0.1	3.7
Energy and Power	-	0.2	-	0.5
Total Annual Costs	1.6	4.5	0.6	8

Effluent Quality (expressed in terms of yearly averages)

	Raw Waste Load	Resulting Effluent Levels (units per 1000 units of product)
B.O.D.	20	
C.O.D.	40	(No specific guidelines)
Suspended Solids	N/A	

*The Spandex contribution is 0.06 thousand cubic meters per day (0.015 MGD); this is approximately 2% of the total flow to be treated.

TABLE VIII-5/1

INDUSTRIAL WASTE TREATMENT MODEL DATA SYNTHETIC POLYMERS PRODUCTION

	EVA Copolymers	Fluorocarbons	Polypropylene Fibers	Polyvinylidene Chloride	Acrylic Resins
Total Industry Discharge					
1000 cubic meters/day (or million gallons/day)					
1972	2.3(0.6)	4.2(1.1)	1.5(0.4)	0.4(0.1)	13.2(3.5)
1977	4.2(1.1)	5.7(1.5)	2.3(0.6)	0.4(0.1)	33.1(8.7)
Quality of Effluents in 1977					
(Expressed in terms of yearly averages)					
Parameters: (in units/1000 units of product)					
BOD_5	0.13	2.3	0.25	NA	NA
COD	1.3	23	1.25	NA	NA
Suspended Solids	0.25	4.5	0.50	NA	NA
Hydraulic Load: 1972-1977					
cu m/kkg (or gal/lb)	8.3(1.0)	92 (18)	16.7(2.0)	NA	NA
Numbers of Companies	5	5	3	4	>4
Percent of Treatment in 1972					
(in percent now treated)					
A. Industrial Pretreatment	100	100	0	100	80
B. Industrial Biological	60	0	0	50	65
C. Municipal	0	100	100	0	20

TABLE VIII-5/2

INDUSTRIAL WASTE TREATMENT MODEL DATA - SYNTHETIC POLYMERS PRODUCTION

	Cellulose Derivatives	Alkyds and Unsaturated Polyesters	Cellulose Nitrate	Polyamides	Polyesters Thermoplastic
Total Industry Discharge					
1000 cubic meters/day (or million gallons/day)					
1972	15.9(4.2)	6.8(1.8)	9.8(2.6)	0.8(0.2)	0.4(0.1)
1977	20.9(5.5)	13.7(3.6)	9.8(2.6)	1.2(0.3)	0.8(0.2)
Quality of Effluents in 1977					
(Expressed in terms of yearly averages)					
Parameters: (in units/1000 units of product)					
BOD_5	NA	0.4	5.0	0.3	0.35
COD	NA	2.0	25	3.0	5.3
Suspended Solids	NA	0.1	4.2	0.2	0.24
Hydraulic Load: 1972-1977					
(cu m/kkg (or gal/lb)	NA	3.2(0.4)	142(17)	6.7(0.8)	2.2(0.95)
Numbers of Companies	3	>14	2	3	3
Percent of Treatment in 1972					
(in percent now treated)					
A. Industrial Pretreatment	100	10	100	100	100
B. Industrial Biological	100	10	40	60	50
C. Municipal	0	90	60	0	0

TABLE VIII-5/3
INDUSTRIAL WASTE TREATMENT MODEL DATA - SYNTHETIC POLYMERS PRODUCTION

	Polyvinyl Butyral	Polyvinyl Ethers	Silicones	Nitrile Barrier Resins	Spandex Fibers
Total Industry Discharge 1000 cubic meters/day (or million gallons/day)					
1972	5.3(1.4)	0.4(0.1)	29.9(7.9)	0.8(0.2)	0.4(0.1)
1977	6.7(1.8)	0.6(0.2)	48.5(12.8)	2.7(0.7)	0.4(0.1)
Quality of Effluents in 1977					
(Expressed in terms of yearly averages)					
Parameters: (in units/1000 units of product)					
BOD_5	NA	NA	10.5	NA	NA
COD	NA	NA	53	NA	NA
Suspended Solids	NA	NA	7.0	NA	NA
Hydraulic Load: 1972-1977					
cu m/kkg (or gal/lb)	NA	NA	233(28)	NA	NA
Numbers of Companies	2	2	4	3	3
Percent of Treatment in 1972					
(in percent now treated)					
A. Industrial	100	70	100	100	100
B. Industrial Biological	25	0	20	70	60
C. Municipal	75	30	0	30	10

SECTION IX

BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE GUIDELINES AND LIMITATIONS

Definition of Best Practicable Control Technology Currently Available (BPCTCA)

Based on the analysis of the information presented in Sections IV to VIII, the basis for BPCTCA is defined herein. Best practicable control technology currently available (BPCTCA) for existing point sources is based on the application of end-of-pipe technology such as biological treatment for BOD_5 reduction as typified by activated sludge, aerated lagoons, trickling filters, aerobic-anaerobic lagoons, etc., with appropriate preliminary treatment typified by equalization, to dampen shock loadings, settling, clarification, and chemical treatment, for removal of suspended solids, oils, other elements, and pH control, and subsequent treatment typified by clarification and polishing processes for additional BOD_5 and suspended solids removal and dephenolizing units for the removal of phenolic compounds. Application of in-plant technology and changes which may be helpful in meeting BPCTCA include segregation of contact process waste from noncontact waste waters, elimination of once-through barometric condensers, control of leaks, and good housekeeping practices.

The best practicable control technology currently available has been found to be capable of generally effecting removal efficiencies of upwards to 85 percent in single-stage biological systems. The design and operating parameters of the biological treatment system may vary from essentially those of a municipal sewage treatment plant to those uniquely tailored to a specific plant waste. The acceptability of many of the waste waters into municipal sewage systems has been established and often proves to be one of the best methods of waste water treatment where suitable pretreatment can be effected and where the synergistic effects of treating with sewage occur. The applicability of biological systems has been proven regardless of the age or size of the manufacturing plant.

Because of the relatively small number of single product waste water treatment plants (much of the industry uses either multi-plant waste water treatment or municipal treatment) the amount of data on which effluent limitations can be based is limited, and it has been necessary to rely

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on analogy and technology transfer for guidelines in some instances. Because of the variabilities inherent in the performance characteristics of industrial waste water treatment plants, especially those affecting the growth of microorganisms such as temperature and variable concentrations, the guidelines have taken into consideration demonstrated unique properties such as high concentrations of COD that can exist in the treated waste waters. The parameters of primary concern are BOD5, COD, and suspended solids. Other parameters such as pH, metals, nitrogenous compounds and specific chemicals such as phenolics are also of concern to the industry.

In Table VII-4 of Section VII the effluent loadings which are currently being attained by the product subcategories for BOD5, COD, and suspended solids are presented. In some instances it was necessary to calculate effluent loadings based on the hydraulic flows emanating from the production plant and the concentrations of the particular parameters in the effluents from a waste water treating plant handling waste water streams from a number of other processes. This procedure was adopted when it was known that a significant fraction of the waste water treatment plant load came from the process under consideration or where the treatability of the waste waters could be expected to be analogous to those of the major product, e.g., the similarity of ethylene-vinyl acetate wastes to low density polyethylene wastes. Using this approach, it was apparent from the results of this work that practicable waste water treatment plants are in operation and that their operational parameters are comparable to those of the resins segment of this industry as well as with biological treatment systems in other industries. It is apparent, therefore, that the most significant factors in establishing effluent limitations guidelines on a basis of units of pollutants per unit of production are (1) the waste water generation rates per unit of production established for an exemplary plant and (2) the concentration levels in the waste waters from the best practicable waste water treatment techniques.

The Guidelines

The effluent limitations guidelines as kg of pollutant per kkg of production (lb/1000 lbs) are based on attainable effluent concentrations and demonstrated waste water flows for each product and process subcategory where a sufficient number of similar products or processes could be identified.

Attainable Effluent Concentrations

Based on the definition of BPCTCA, the following long-term average BOD5 and suspended solids concentrations were used as a basis for the guidelines.

	BOD5 mg/liter	TSS mg/liter
Major Subcategory I	15	30
Major Subcategory II	20	30
Major Subcategory III	45	30
Major Subcategory IV	75	30

The BOD5 and total suspended solids concentrations are based on observed or reported performance of water treatment plants. In many subcategories of this segment of the plastics and synthetics industry, the in-place waste water technology and treatment levels are inadequate. By proper design and application of the defined technologies, the levels proposed are attainable as demonstrated by other subcategories within this industry and other industries such as organics and petroleum refining. The COD limitations were included in the proposed regulation because COD is a measure of the chemical by-product waste of the manufacturing process and falls under the definition of pollutant contained in the Act [§502(6)]. All of the proposed 1977 COD limitations were non-controlling as to technology. That is, the COD limitations were such that adequate removal of BOD5 will usually result in adequate removal of COD. The proposed numbers were derived from data showing the removal of COD which accompanies reduction of BOD5 to the levels proposed in the effluent limitations for each subcategory. A plant which is achieving the BOD5 removal required by the regulations need not use any additional technology to meet the proposed COD levels for BPCTCA. The presence of a COD limitation nonetheless fulfills an important function by requiring adequate handling and treatment of discarded (bad) batches of reactants and products, so as to avoid shock or peak COD loadings which would be inadequately treated but would not be discovered by a BOD5 analysis. Also, the COD test is a much quicker and more convenient test for the presence of oxygen demanding pollutants than is the BOD5 test. However, since the proposed BPCTCA (1977) COD limits are liberal and would be easily attainable if the BOD5 limits are met, they are being dropped as a limitation parameter for BPCTCA (1977).

The COD characteristics of the polymer segment of the synthetics and plastics industry vary significantly from

TABLE IX-1

COD/BOD$_5$ RATIOS

	Raw	Treated
Acrylic Resins	1.3 - 2.7	1.4 - 3.3
Alkyd and Unsaturated Polyester Resins	2 - 3.7	5.2
Cellulose Derivatives	2.4 - 4.2	-
Cellulose Nitrate	2.5 - 4.1	-
Ethylene-Vinyl Acetate/ Polyethylene	4.2	5.0
Polytetrafluoroethylene	1.8	-
Nitrile Barrier Resins	2.3 - 2.9	-
Polyesters (thermoplastic)	-	-
Polypropylene Fibers	3.2 - 3.8	-
Polyvinyl Butyral	1 - 4.8	4.6 - 23
Polyvinyl Ether	-	-
Polyvinylidene Chloride	-	-
Silicones	2.5	5.1

product to product and within an individual plant over time. The ratio of COD and BOD_5 in the raw waste water and treated waste waters are shown in Table IX-1 and range from a low of 1.0 to a high of 23. There is a real need for more data in all sections of the polymer segment of the plastics and synthetics industry to provide a better understanding of the waste water loads, the treatability of the waste waters and, in particular, a better understanding of the nature of the COD component and methods for its reduction. In order to promote the collection of data on the oxygen demanding parameters of BOD_5, COD and TOC (total organic carbon), the Agency is planning to require that a majority of the plants in each subcategory monitor their raw waste loads and treated effluents for BOD_5, COD and TOC. This data will be collected for a reasonable period at which time the Agency will consider revising the limitations and standards.

In applying the BOD_5 limitation guidelines, if a plant can show a direct relationship over a long period of time between BOD_5, COD and TOC (total organic carbon), or TOD (total oxygen demand), the parameter measurement of the COD, TOC, or TOD could be substituted for BOD_5 if the COD, TOC, or TOD limitations are set such that the BOD_5 limitation is not exceeded.

Although guidelines are not established for phenolics in the polymers segment of the industry, wherever phenolic compounds are identified their removal should remain the same as for the resins portion of the industry, i.e., an attainable concentration level of 0.5 mg/liter monthly limit as demonstrated by dephenolizing units (42) activated carbon (13, 14, 35, 39) or biological degradation.

The removal of oil and grease is based on 30 mg/liter monthly limit attainable concentrations as demonstrated by various physical and chemical processes in other industries (35).

The removal of fluorides is based on an attainable concentration of 20 mg/liter by lime precipitation as used in effluent guidelines for the iron and steel industry. It should be noted that the fluoride level shown for the polytetrafluoroethylene (PTFE) subcategory applies to the fluoride content of the effluent from the water scrubber in the TFE monomer process only, not to the total waste water discharge from the overall PTFE process. The scrubber effluent, a dilute HCl solution, is the only significant source of fluoride discharge from the PTFE process. At all present PTFE manufacturing operations, this scrubber effluent is segregated from other waste waters and disposed of by various means, including deep well, ocean dumping, or off-site contract methods. The waste water flow from the scrubber amounts to 1/5 or less of the total waste water generated by the process. The guideline for fluoride was derived on the basis of 20 mg/l attainable concentration and a scrubber effluent flow of 3500 gal/1000 lbs product.

Cyanides, mercury, and cadmium limitations should be consistent with the limitations of toxic and hazardous chemicals prepared in the Federal Register of December 27, 1973(38).

The removal of copper and lead is based on an attainable concentration of 0.5 mg/liter as demonstrated by alkaline chemical precipitation (35).

The copper limitations for the silicone production facilities were established in the following manner.

1. Precipitation of soluble copper by means of lime treatment was selected as the most applicable treatment technology. It has been shown to be capable of achieving effluent copper concentrations of less than 0.5 mg/liter.

2. It was assumed that no internal waste stream segregation would be employed and that the total volume of waste water emanating from the production facilities would be subjected to the above lime treatment.

3. The average waste flows in terms of gal/1000 lbs were used for the silicones plants by averaging the values of the reported range of waste flows.

4. The maximum average for a 30-day period for BPCTCA was then developed using the average waste flows established in (3) in conjunction with the demonstrated 0.5 mg/liter copper effluent using lime treatment. The maximum average daily limitations were taken as twice the average 30-day limitations.

Since the lime treatment process theoretically removes copper to a fixed solubility limit rather than removing a certain percentage of the influent copper, the quantity of copper in the raw waste water is of no consequence with respect to the attainable effluent copper concentration. Thus, the fact that different silicone production facilities may produce waste waters with vastly varying quantities of copper is irrelevant with respect to the established limitations. The net result is that the limitations on copper, in pounds/1000 pounds of product, are dependent on hydraulic load attainable. In one respect, the copper limitations are actually conservative in favor of the industry, because it was not presumed that copper-bearing waste streams would be segregated from other waste streams for treatment, a practice which would reduce the total quantity of copper in the effluent.

Demonstrated Waste Water Flows

The waste water flow basis for BPCTCA is based on demonstrated waste water flows found within the industry. Because of the small number of manufacturing plants in most categories, and/or the limited data base, the demonstrated waste water flows shown in Table IX-2 were based on engineering judgments taking into consideration reported flows and other assessments such as the type of operation, nature of housekeeping, and apparent operational attention to good water conservation practices. The demonstrated waste water flows are based (where possible) on direct contact process water only and do not include boiler water blowdown, water treatment regeneration wastes, cooling water blowdown, and any other waters deriving from utilities and supporting services. The resultant wastewater flows used for calculating the limitation guidelines were reasonable and representative of what most plants in each subcategory are or should be achieving. It is essential to take into consideration the fact that waste water flow is often an integral part of the basic process design and operation of the process and plant and, therefore, would be subject to significant reduction only at considerable expense. Although generally the unit hydraulic loads are larger for older plants, the availability of water influences the design as does the designer's philosophy and the company's operating procedures. No simple formula has been found for relating hydraulic load to plant age, size or location.

Statistical Variability of a Properly Designed and Operated Waste Treatment Plant

The effluent from a properly designed and operated treatment plant changes continually due to a variety of factors. Changes in production mix, production rate, climatic conditions, and reaction chemistry influence the composition of raw waste load and, therefore, its treatability. Changes in biological factors influence the efficiency of the treatment process. A common indicator of the pollution characteristics of the discharge from a plant is the long-

TABLE IX-2

DEMONSTRATED WASTEWATER FLOWS

	WASTEWATER FLOW RATES	
	cum/kkg	gal/1000 lbs
Alkyd Molding Compounds and Unsaturated Polyester Resins	3.3	400
Cellulose Nitrate	142	17,000
Ethylene-Vinyl Acetate	8.34	1,000
Polytetrafluoroethylene	150	18,000
Polyamides (Nylon 6/12 only)	6.7	800
Polyester Resins (Thermoplastic)	7.9	950
Polypropylene Fibers	16.7	2,000
Silicones		
Fluids	10.4	1,250
Greases, Emulsions, Rubbers, and Resins	133	16,000
Coupling Agents	83.4	10,000

term average of the effluent load. The long-term (e.g., design or yearly) average is not a suitable parameter on which to base an enforcement standard. However, using data which show the variability in the effluent load, statistical analyses can be used to compute short-term limits (monthly or daily) which should not be exceeded, provided that the plant is designed and run in the proper way to achieve the desired long-term average load. It is these short-term limits on which the effluent guidelines are based.

In order to reflect the variabilities associated with properly designed and operated treatment plants for each of the major subcategories as discussed above, a statistical analysis was made of plants where sufficient data was available to determine these variances for day-to-day and month-to-month operations. The standard deviations for day-to-day and month-to-month operations were calculated. For the purpose of determining effluent limitation, a variability factor was defined as follows:

Standard deviation = Q monthly, Q daily
Long-term average (yearly or design) = x
Variability factor = y monthly, y daily

$$y \text{ monthly} = \frac{x + 2Q \text{ monthly}}{x}$$

$$y \text{ daily} = \frac{x + 3Q \text{ daily}}{x}$$

The variability factor is multiplied by the long-term yearly average to determine the effluent limitations guideline for each product subcategory. The monthly effluent limitations guideline is calculated by use of a variability factor based on two standard deviations and is only exceeded 2 to 3 percent of the time for a plant that is attaining the long-term average. The daily effluent limitations guideline is calculated by the use of a variability factor based on three standard deviations and is exceeded only 0.0-0.5 percent of the time for a plant that is attaining the long term average. Any plant designed to meet the monthly limits should never exceed the daily limits. The data used for the variability analysis came from plants under voluntary operation. By the application of mandatory requirements, the effluent limitations guidelines as discussed in this paragraph should never be exceeded by a properly designed and operated waste treatment facility.

The variability factors in Table IX-3 are based on the data obtained in the synthetic resin segment (16) of the plastics and synthetics industry.

The variability factors for suspended solids removal are the same as used in the resins segment of the industry, i.e., a monthly variability of 2.2 and a daily variability of 4.0.

The variability factors recommended for total chromium, phenolics, copper, lead, and oils and grease are based on the monthly limits and a variability factor of 2.0 for the daily maximum.

Based on the factors discussed in this section, the effluent limitations guidelines for BPCTCA are presented in Tables IX-4 and IX-5.

TABLE IX-3

VARIABILITY FACTORS FOR BOD_5

	BOD_5 Monthly	Variability Factors Daily
Major subcategory I	1.6	3.1
" " II	1.8	3.7
" " III	2.2	4.0
" " IV	2.2	4.0

TABLE IX-4

BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE EFFLUENT LIMITATIONS GUIDELINES
[kg/kkg (lb/1000 lb) of production]

Foot-note No.	Subcategory	BOD_5		SUSPENDED SOLIDS	
		Maximum Average of Daily Values for Any Period of Thirty Consecutive Days	Maximum for Any One Day	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days	Maximum for Any One Day
1	Ethylene-Vinyl Acetate Copolymers	0.20	0.39	0.55	1.0
2	Polytetrafluoroethylene	3.6	7.0	9.9	18.0
3	Polypropylene Fiber	0.40	0.78	1.1	2.0
4	Polyvinylidene Chloride	No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote	
5	Acrylic Resins	"	"	"	"
6	Cellulose Derivatives	"	"	"	"
7	Alkyds and Unsaturated Polyester Resins	0.33	0.60	0.22	0.40
8	Cellulose Nitrate	14	26	9.4	17
9	Polyamides (Nylon 6/12 only)	0.66	1.20	0.44	0.80
10	Polyester Resins (thermoplastic)	0.78	1.4	0.52	0.95
11	Polyvinyl Butyral	No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote	
12	Polyvinyl Ethers	"	"	"	"
13	Silicones				
	Fluid	1.0	1.9	0.69	1.25
	Greases, Emulsions, Rubbers, Resins	13.2	24	8.8	16
	Coupling Agents	8.2	15	5.4	10
14	Nitrile Barrier Resins	No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote	
15	Spandex Fibers	"	"	"	"

FOOTNOTES FOR TABLES IX-4 and IX-5

1. Ethylene-Vinyl Acetate (EVA) Copolymer. Two of the five known producers were contacted. All plants are located at polyethylene production facilities. Water use and wastewater characteristics for EVA are essentially identical to those for low density polyethylene. However, an emulsion polymerization process is known and produces a distinctly different waste load which is essentially that of polyvinyl acetate emulsion polymerization reported in EPA 440/1-73/010. Both multi-plant and municipal sewage treatment is used.

2. Polytetrafluoroethylene. Three of the seven manufacturing plants were visited. A wide range of products are produced. The most important is polytetrafluoroethylene (PTFE) and these guidelines are recommended for PTFE granular and fine powder grades only. The wastewater discharges differ considerably depending upon the process recovery schemes for hydrochloric acid and the disposal of selected streams by deep well, ocean dumping or off-site contract methods. The use of ethylene glycol in a process can significantly affect the waste loads. Fluoride concentrations in untreated wastewaters are generally below levels attainable by alkaline precipitation.

3. Polypropylene Fibers. Two of the three producers were contacted. The volumetric flow ranges per unit of production vary widely depending upon the type of cooling system used. The waste loads are for plants where selected concentrated wastes are segragated and disposed of by landfilling, etc. Primary treatment at one plant site was observed while the other plant discharges to a municipal sewage system.

4. Polyvinylidene Chloride. The two major manufacturers were contacted. Both plant sites send wastewaters to multi-plant treatment plants of which the polyvinylidene chloride is a small portion. Consequently, there was insufficient data to develop recommended guidelines.

5. Acrylic Resins. Three of the four manufacturers were contacted. Large numbers of product grades are produced by bulk, solution, suspension and emulsion polymerization. The widely varying hydraulic loads for the large number of products in addition to treatment of the wastewaters by multi-plant wastewater treatment facilities prohibited obtaining sufficient meaningful data to recommend effluent limitation guidelines.

6. Cellulose Derivatives. Cellulose derivates investigated included ethyl cellulose, hydroxyethyl cellulose, methyl cellulose and carboxymethyl cellulose. Wide variations in unit flow rates for two plants producing the same product, differences in manufacturing techniques and the availability of data prevented recommending guidelines. The wastewaters from the three manufacturers are being treated in multi-plant wastewater treatment facilities or will enter municipal sewage systems.

7. Alkyds and Unsaturated Polyester Resins. Six carefully selected plants were visited to provide a cross-section of the industry for size of operation, type of manufacturing process and wastewater treatment methods. Hydraulic loads vary widely depending upon the process designs. Similarly, raw waste loads vary widely because some plants segragate wastes for disposal in other manners. Generally, the industry discharges wastewaters into municipal sewage systems and should continue. Also, the type of air pollution control, e.g. combustion or scrubbing, has a significant effect on the wastewater loads. The recommended guidelines are for plants having their own wastewater treatment system - a very infrequent occurrence.

8. Cellulose Nitrate. The two major manufacturers of the four manufacturers were contacted. These wastes require pH control and contain large amounts of nitrates. One plant discharges to a municipal sewage system while the other goes into a multi-plant treatment complex.

9. Polyamides. Various polyamides are produced but only Nylon 6/12 produces significant amounts of wastewater, e.g. Nylon 11 uses no process water. Consequently, the guidelines are restricted to Nylon 6/12 and were developed on the basis of similarity with waste loads from Nylon 66 production.

10. Polyester Thermoplastic Resins. There are three manufacturers, two of which produce poly(ethylene, terephthalate) in quantities less than 2% of their total thermoplastic production. The guidulines are recommended for poly(ethylene terephthalate) since the other product poly(butylene terephthalate) is produced at only one plant and the wastewater goes into a municipal sewage system, so no data on performance could be obtained.

11. Polyvinyl Butyral. Of three production sites,two have processes beginning with vinyl acetate monomer which generates much larger wastewater volumes than the process beginning with polyvinyl alcohol. Since the manufacturing sites where production starts with a monomer discharge into municipal sewage systems, there was no data available. Consequently, there are no recommended guidelines since they would be tantamount to establishing a permit for the direct discharger production site.

12. Polyvinyl ethers. The three present plants use different processes each of which produces several grades of product. The different chemical compositions used in both bulk and solution polymerization processes and the lack of data on both raw and treated wastewaters prevented establishing guidelines. The wastewaters are presently sent to either multi-plant treatment facilitie or municipal sewage systems.

13. Silicones. Four companies manufacture silicones at five locations. Three plants were visited and data were obtained from all plants. The major processing steps at the five plants are shown below.

Major Processes at Five Silicone Plants

Plant No.	1	2	3	4	5
CH_3Cl	x		x	x	
Chlorosilane prod.	x	x	x	x	x
Hydrolysis	x	x	x	x	x
Fluids, greases, emulsions prod.	x	x	x	x	x
Resin production	x	x	x		
Elastomer production	x	x	x		x
Specialties prod.*	x	x	x		
Fumed silica prod.			x		
HCl production					x

* e.g. surfactants, fluorinated silicones, coupling agents, and other materials.

Based on the manufacturing process, the waste water flows and the raw waste loads, the plants 1, 2, 3 and 5 were designated as multi-product plants while 4 was designated as a fluid product plant.

14. Nitrile Barrier Resins. Commercial scale production and sale of these resins has not yet begun. The companies expected to have production facilities were contacted, and two provided estimates of raw waste loads. Because of the lack of demonstrated flows and raw waste loads, it was impossible to establish effluent guideline limitations.

15. Spandex Fibers. Three manufacturers each produce Spandex fibers by significantly different processes. These are dry, wet and reaction spinning methods. Because of limited data on raw waste loads and because each plant operates a different process, it was impossible to establish meaningful guidelines.

TABLE IX-5

BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE EFFLUENT LIMITATIONS GUIDELINES
(Other Elements and Compounds)

Product	Parameter	kg/kkg (lbs/1000 lbs of production)	
		Maximum average of daily values for any period of thirty consecutive days	Maximum For Any One Day
Alkyds and unsaturated polyester resins			
	Mercury	Toxic and hazardous chemicals guidelines to apply	
Polytetrafluoroethylene	Fluorides	0.6	1.2
Spandex fiber	Cyanides	Toxic and hazardous chemicals guidelines to apply	
Nitrile barrier resins	Cyanides	" " "	" "
Polypropylene fibers	Oils & grease	0.5	1.0
Silicones			
Fluids	Copper	0.005	0.010
Greases, Emulsions, Rubbers and Resins	Copper	0.067	0.13
Coupling Agents	Copper	0.042	0.084
Polyester resins (Thermoplastic)	[illegible]mium	T[illegible] and hazardous chemical guidel t[illegible]ly	

SECTION X

BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE

Definition of Best Available Technology Economically Achievable (BATEA)

Based on the analysis of the information presented in Sections IV to VIII, the basis for BATEA is defined below.

Best available technology economically achievable (BATEA) for existing point sources is based on the best in-plant practices of the industry which minimize the volume of waste generating water as typified by segregation of contact process waters from noncontact waste water, maximum waste water recycle and reuse, elimination of once-through barometric condensers, control of leaks, good housekeeping practices, etc., and end-of-pipe technology, for the further removal of suspended solids and other elements typified by granular media filtration, chemical treatment, etc., and further COD removal as typified by the application of adsorption processes such as activated carbon and adsorptive flocs, and incineration for the treatment of highly concentrated small volume wastes and additional biological treatment for further BOD_5 removal when needed.

Best available technology economically achievable can be expected to rely upon the usage of those technologies which provide the greatest degree of pollutant control per unit expenditure. Historically, this has been the approach to the solution of any pollution problem -- as typified by the mechanical and biological treatment used for removal of solids and biochemically active dissolved substances, respectively. At the present stage of development, it is technologically possible to achieve complete removal of pollutants from waste water streams. The economic impact of doing this must be assessed by computing cost benefits to specific plants, entire industries, and the overall economy. The application of best available technology will demand that the economic achievability be determined, increasingly, on the basis of considering water for its true economic impact. Unlike best practicable technology, which is readily applicable across the industry, the selection of best available technology economically achievable becomes uniquely specific to each process and in each plant. Furthermore, the human factors associated with conscientious operation and meticulous attention to detail become increasingly important if best available technology is to achieve its potential for reducing the emission of pollutants from industrial plants.

The Guidelines

Achievable Effluent Concentrations

Suspended Solids

The removal of suspended solids from waste water effluent is based on well-understood technology developed in the chemical process industries and water treatment practices. Application of filtration to the effluents from waste water treatment plants has not been applied often, although its feasibility has been demonstrated in projects sponsored by the Environmental Protection Agency. The operation of filtration systems, such as the in-depth granular media filter for waste waters, is not usually as straightforward as it is in water treatment. This is due, especially, to the biological activity still present in waste waters and sometimes to the nature of the colloidal particles from the process.

Long residence time lagoons with their low flow-through rates are often effective means for the removal of suspended solids, although the vagaries of climatic conditions, which can cause resuspension of settled solids, and the occurrence of algal growth can cause wide fluctuations in the concentration of suspended solids in the effluent. Although technology is available for reducing suspended solids in effluents to very low levels (approaching a few mg/liter), the capital and operating cost for this technology adds significantly to waste water treatment costs. The concentration basis for BATEA is 10 mg/liter for all product and process subcategories (1, 15, 35). This concentration is achievable by use of filtration techniques including mixed media filtration. Mixed media filtration is a pollution control technique which is well established and is currently used with considerable success in a number of treatment works - including municipal systems and waste treatment systems used in the petroleum industry. The wastes from biochemical treatment systems consists mostly of microbial cells regardless of the original source of the raw wastes. Microbial cells have similar solids removal characteristics. While it has not been demonstrated in the plastics and synthetics industry, the success shown in other uses convinces the Agency that mixed media filtration is fully adaptable to this industry and will achieve the effluent concentration required, if necessary.

Oxygen-Demanding Substances

Removal of biochemical-oxygen-demanding substances to concentration levels less than the range proposed for municipal sewage treatment plants will require the utilization of physical-chemical processes. It is expected, however, that the chemical-oxygen-demanding substances will present a far greater removal problem than BOD_5 because the biochemically treated waste water will have proportionally much higher ratios of COD to BOD_5 than entered the waste water treatment plant. In the case of a few polymer products, the waste waters may contain substances giving a significant COD concentration while being resistant to biological degradation under the most optimum conditions. To reduce the COD in a treated effluent, it will be necessary either to alter processes so that nonbiodegradable fractions are minimized or attempt to remove these substances by some method of waste water treatment. Both of these approaches may be difficult. Alteration of processes so that they produce less refractory wastes may not be possible within the constraints of the required chemical reactions. However, reduction in the quantities of wastes generated by spills, leaks, and poor housekeeping practices can contribute significantly to reducing the total COD discharges, especially where a large fraction of the pollutants are refractory to biological degradation. Consequently, one of the first steps in a program to reduce emissions should be a thorough evaluation of the process operation alternatives and techniques for preventing pollutants from entering the waste water streams.

In other methods for removal of oxygen demanding substance, adsorption by surface-active materials, especially activated carbon, has gained preeminence. Although the effectiveness of activated carbon adsorption has been well demonstrated for removing BOD_5 and COD from the effluents of conventional municipal sewage treatment plants, its effectiveness for the removal of the complex chemical species found in the waste water of this industry can be expected to be highly specific. Evidence of the low adsorption efficiency of activated carbon for a number of different chemical species is beginning to appear in the technical literature. However, the only way to determine if activated carbon adsorption is an effective method for removing COD is to make direct determinations in the laboratory and in pilot plants. In some instances, activated carbon adsorption may be used to remove substances selectively (for example, phenols) prior to treatment by other methods. Although activated carbon adsorption is proving to be a powerful tool for the removal of many chemical oxygen demanding and carbonaceous substances from waste water streams, it is not a panacea. Its use must be evaluated in terms of the high capital and operating costs, especially for charcoal replacement and energy, and the benefits accrued.

Removal of carbonaceous and oxygen demanding substances can sometimes be achieved through oxidation by chlorine, ozone, permanganates, hypochlorites, etc. However, not only must the cost benefits of these be assessed but certain ancillary effects, such as (1) the production of chlorinated by-products which may be more toxic than the substance being treated, (2) the addition of inorganic salts, and (3) the toxic effects of the oxidants themselves, must be taken into account. Consequently, when chemical oxidation is employed for removal of COD, it may be necessary to follow the treatment with another step to remove the residuals of these chemicals prior to discharge to receiving waters.

Degradation of oxygen demanding substances may take place slowly in lagoons if sufficiently long residence time can be provided. If space is available, this may be an economic choice. Also, the use of land irrigation, or the "living filter" approach to water purification, is receiving selected attention. Ultra-filtration and reverse osmosis, both of which are membrane techniques, have been shown to be technically capable of removing high molecular species, but they have not been shown to be operationally and economically achievable. With these techniques, the molecular distribution of the chemical species determines the efficiency of the separation. They probably have limited potential in the plastics and synthetics industry, due to the particular spectrum of molecular weights occurring in the waste waters.

The concentration basis for BATEA for COD is either 130 mg/liter as demonstrated in an activated carbon plant (4) in the plastics and synthetics industry, or that concentration documented by plants in Table VII-3 as attainable in biological treatment systems or retention lagoons. The BOD_5 concentrations which are attainable by biological treatment plants as expressed in the better waste water treatment plants as presented in data from the synthetic resins segment (16) of this industry, are 15 mg/liter for Major Subcategory I and II products and 25 mg/liter for Major Subcategory III and IV products. The removal of fluorides is on the same basis as for BPCTCA as outlined in Section IX. Similarly, the limitations on mercury, cadmium, and cyanides should be those prescribed for toxic and hazardous chemicals.

The removal of oils and greases to a concentration of 10 mg/liter, copper to a concentration of 0.25 mg/liter, and lead to 0.03 mg/liter is based on the concentrations attainable (35) when filtration is used for solids removal.

Waste Load Reduction Basis

The waste load recommendation for BATEA is based on overall loading reduction through the use of the best achievable concentrations and the reduction of waste water flows from BPCTCA to a level between the BPCTCA waste water flows and the verified BADT waste water flows as described in Section XI. The wastewater flows are given in Table X-1. The wastewater flows used for calculating BATEA are reasonable estimates of reductions which industry should be able to achieve by 1983, using the various methods of wastewater flow reduction and recycle as outlined in sections VII and IX.

TABLE X-1

BATEA Waste Water	Flow Rates	
	cum/kkg	gal/1000 lbs
Alkyd Molding Compounds and Unsaturated Polyester Resins	1.83	220
Cellulose Nitrate	125	15,000
Ethylene-Vinyl Acetate	7.92	950
Polytetrafluoroethylene	91.7	11,000
Polyamides (Nylon 6/12 only)	6.67	800
Polyester Resins (Thermoplastic)	7.92	950
Polypropylene Fibers	9.17	1,100
Silicones		
fluid products	10.4	1,250
multi products	133	16,000

Increased efficiency in the utilization of water combined with closer operational control to prevent pollutants from entering waste water streams have the greatest promise for reducing the amounts of pollutants discharged from waste water treatment plants. While the reduction of water usage may directly reduce the total emission of certain pollutants, it may mean that advanced waste water treatment systems become more economically feasible.

Variability

The variability factor for BATEA guidelines is based on the variability determined by data from BPCTCA. Both the monthly and daily variabilities are based on two standard deviations. As technology and plant operations improve, it is expected that these variabilities will become more stringent. The BOD_5, COD, and TSS variabilities are presented in Table X-2. The TSS factors are based on data obtained from multi-media filters used in the petroleum refining industry. The other parameters are based on the achievable concentration for monthly maximum and a variability factor of 2 to determine the daily maximum.

TABLE X-2

Variability Factors BATEA

	BOD_5 and COD		TSS	
	Monthly	Daily	Monthly	Daily
Major Subcategory I	1.6	2.4	1.7	2.0
Major Subcategory II	1.8	2.8	1.7	2.0
Major Subcategory III	2.2	3.0	1.7	2.0
Major Subcategory IV	2.2	3.0	1.7	2.0

Based on the factors discussed in this section, the Effluent Limitations Guidelines for Best Available Technology Economically Achievable, BATEA, are presented in Tables X-3 and X-4.

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TABLE X-3

BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE EFFLUENT LIMITATIONS GUIDELINES
[kg/kkg (lb/1000 lb) of production]

Subcategory	BOD_5		COD		SUSPENDED SOLIDS	
	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days	Maximum for Any One Day	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days	Maximum for Any One Day	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days	Maximum for Any One Day
Ethylene-Vinyl Acetate Copolymers	0.19	0.29	1.65	2.48	0.14	0.26
Polytetrafluoroethylene	2.2	3.3	4.0	5.9	1.6	2.4
Polypropylene Fiber	0.22	0.33	0.40	0.59	0.16	0.18
Polyvinylidene Chloride	No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote	
Acrylic Resins	"	"	"	"	"	"
Cellulose Derivatives	"	"	"	"	"	
Alkyds and Unsaturated Polyester Resins	0.10	0.14	0.52	0.74	0.03	0.04
Cellulose Nitrate	6.9	9.4	34	47	2.1	2.8
Polyamides (Nylon 6/12 only)	0.37	0.50	1.9	2.6	0.11	0.13
Polyester Resins (thermoplastic)	0.44	0.59	2.3	3.1	0.14	[illegible]
Polyvinyl Butyral	No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote	
Polyvinyl Ethers	"	"	"	"	"	"
Silicones						
Fluid	0.57	0.28	3	4	0.21	0.18
Greases, Emulsions, Rubbers, Resins, and Coupling Agents	6.4	8.8	33.4	45.5	2.0	2.3
Nitrile Barrier Resins	No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote	
Spandex Fibers	"	"	"	"	"	"

[illegible]S FOR TABLES X-3 and X-4

1. **Ethylene-Vinyl Acetate (EVA) Copolymer**. Two of [illegible] known producers were contacted. All plants are [illegible] at polyethylene production facilities. Water use a[illegible] wastewater characteristics for EVA are essentially identical to those for low density polyethylene. However, an emulsion polymerization process is known and produces a distinctly different waste load which is essentially that of polyvinyl acetate emulsion polymerization reported in EPA 440/1-73/010. Both multi-plant and municipal sewage treatment is used.

2. **Polytetrafluoroethylene**. Three of the seven manufacturing plants were visited. A wide range of products are produced. The most important is polytetrafluoroethylene (PTFE) and these guidelines are recommended for PTFE granular and fine powder grades only. The wastewater discharges differ considerably depending upon the process recovery schemes for hydrochloric acid and the disposal of selected streams by deep well, ocean dumping or off-site contract methods. The use of ethylene glycol in a process can significantly affect the waste loads. Fluoride concentrations in untreated wastewaters are generally below levels attainable by alkaline precipitation.

3. **Polypropylene Fibers**. Two of the three producers were contacted. The volumetric flow ranges per unit of production vary widely depending upon the type of cooling system used. The waste loads are for plants where selected concentrated wastes are segragated and disposed of by landfilling, etc. Primary treatment at one plant site was observed while the other plant discharges to a municipal sewage system.

4. **Polyvinylidene Chloride**. The two major manufacturers were contacted. Both plant sites send wastewaters to multi-plant treatment plants of which the polyvinylidene chloride is a small portion. Consequently, there was insufficient data to develop recommended guidelines.

5. **Acrylic Resins**. Three of the four manufacturers were contacted. Large numbers of product grades are produced by bulk, solution, suspension and emulsion polymerization. The widely varying hydraulic loads for the large number of products in addition to treatment of the wastewaters by multi-plant wastewater treatment facilities prohibited obtaining sufficient meaningful data to recommend effluent limitation guidelines.

6. **Cellulose Derivatives**. Cellulose derivates investigated [illegible]yl included ethyl cellulose, hydroxyethyl cellulose, cellulose and carboxymethyl cellulose. Wide variations in unit flow rates for two plants producing the same product, differences in manufacturing techniques and the availability of data prevented recommending guide[illegible] The wastewaters from the three manufacturers are being treated in multi-plant wastewater treatment [illegible]ilities or will enter municipal sewage systems.

[illegible] [illegible]s and Unsaturated Polyester Resins. Six carefully [illegible]cted plants were visited to provide a cross-section [illegible] the industry for size of operation, type of manufacturing process and wastewater treatment methods. Hydraulic loads vary widely depending upon the process designs. Similarly, raw waste loads vary widely because some plants segragate wastes for disposal in other manners. Generally, the industry discharges wastewaters into municipal sewage systems and should continue. Also, the type of air pollution control, e.g. combustion or scrubbing, has a significant effect on the wastewater loads. The recommended guidelines are for plants having their own wastewater treatment system - a very infrequent occurrence.

8. **Cellulose Nitrate**. The two major manufacturers of the four manufacturers were contacted. These wastes require pH control and contain large amounts of nitrates. One plant discharges to a municipal sewage system while the other goes into a multi-plant treatment complex.

9. **Polyamides**. Various polyamides are produced but only Nylon 6/12 produces significant amounts of wastewater, e.g. Nylon 11 uses no process water. Consequently, the guidelines are restricted to Nylon 6/12 and were developed on the basis of similarity with waste loads from Nylon 66 production.

10. **Polyester Thermoplastic Resins**. There are three manufacturers, two of which produce poly(ethylene, terephthalate) in quantities less than 2% of their total thermoplastic production. The guidelines are recommended for poly(ethylene terephthalate) since the other product poly(butylene terephthalate) is produced at only one plant and the wastewater goes into a municipal sewage system, so no data on performance could be obtained.

11. **Polyvinyl Butyral**. Of three production sites, two have processes beginning with vinyl acetate monomer which generates much larger wastewater volumes than the process beginning with polyvinyl alcohol. Since the manufacturing sites where production starts with a monomer discharge into municipal sewage systems, there was no data available. Consequently, there are no recommended guidelines since they would be tantamount to establishing a permit for the direct discharger production site.

12. **Polyvinyl ethers.** The three [illegible]nt plants use different processes each of which [illegible]ces several grades of product. The different [illegible] compositions used in both bulk and solution [illegible]zation processes and the lack of data on both raw [illegible]ted wastewaters prevented establishing guide[illegible] The wastewaters are presently sent to eithe[illegible] [illegible]ant treatment facilitie or municipal sewage sys[illegible]

13. **Silicones**. Four companies manufacture silicones at five locations. Three plants were visited and data were obtained from all plants. The major processing steps at the five plants are shown below.

Major Processes at Five Silicone Plants

Plant No.	1	2	3	4	5
CH_3Cl	x		x	x	
Chlorosilane prod.	x	x	x	x	x
Hydrolysis	x	x	x	x	x
Fluids, greases, emulsions prod.	x	x	x	x	x
Resin production	x	x	x		
Elastomer production	x	x	x		x
Specialties prod.*	x	x	x		
Fumed silica prod.			x		
HCl production					x

* e.g. surfactants, fluorinated silicones, coupling agents, and other materials.

Based on the manufacturing process, the waste water flows and the raw waste loads, the plants 1, 2, 3 and 5 were designated as multi-product plants while 4 was designated as a fluid product plant.

14. **Nitrile Barrier Resins**. Commercial scale production and sale of these resins has not yet begun. The companies expected to have production facilities were contacted, and two provided estimates of raw waste loads. Because of the lack of demonstrated flows and raw waste loads, it was impossible to establish effluent guideline limitations.

15. **Spandex Fibers**. Three manufacturers each produce Spandex fibers by significantly different processes. These are dry, wet and reaction spinning methods. Because of limited data on raw waste loads and because each plant operates a different process, it was impossible to establish meaningful guidelines.

TABLE X-4

BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE EFFLUENT LIMITATIONS GUIDELINES
(Other Elements and Compounds)

Product	Parameter	kg/kkg (lbs/1000 lbs of Production)	
		Maximum average of daily values for any period of thirty consecutive days	Maximum For Any One Day
Alkyds and unsaturated polyester resins			
	Mercury	Toxic and hazardous chemicals guidelines to apply	
Polytetrafluoroethylene	Fluorides	0.6	1.2
Spandex fibers	Cyanides	Toxic and hazardous chemicals guidelines to apply	
Nitrile barrier resins	Cyanides	" " "	" "
Polypropylene fibers	Oils and grease	0.092	0.18
Silicones			
Fluids	Copper	.0026	.0052
Greases, Emulsions, Rubbers, Resins and Coupling Agents	Copper	.029	.058
Polyester resins (thermoplastic)	[illegible]ium	[illegible] and hazardous chemicals guidelines to apply	

SECTION XI

NEW SOURCE PERFORMANCE STANDARDS
BEST AVAILABLE DEMONSTRATED TECHNOLOGY

Definition of New Source Performance Standards Best Available Demonstrated Technology (NSPS-BADT)

Based on the analysis of the information presented in Sections IV to VIII, the basis for NSPS-BADT is defined below.

Best available demonstrated technology (BADT) for new source performance standards (NSPS) is based on BPCTCA, the maximum possible reduction of process waste water generation along with the application of solids removal operations such as granular media filtration and chemical treatment for additional suspended solids and other element removal as well as additional biological treatment for further BOD_5 removal as needed.

The Standards

Achievable Effluent Concentration

The concentration basis for NSPS-BADT is the same as that for BATEA for BOD_5, TSS, oil and grease, copper and fluoride. The COD concentration basis for NSPS-BADT is based on the concentrations which were attainable in observed biological treatment plants or retention lagoons as expressed in Table VII-3, or were rationally transferable from similar type products. In cases where attainable concentrations were not available as long term or transferable data, COD is not required as a standard.

Waste Load Reduction Basis

The waste water flow basis for NSPS-BADT is based on the lowest verified flows associated with each product. Use of the lowest verified existing waste water flows for calculation of new source standards is fully justified since a new plant can be planned and designed for the lower flows which are currently being demonstrated by plants within each subcategory. The product specific waste water flows are summarized in Table XI-1.

It is apparent that effluent limitations standards requiring significant reductions over that attainable by best practicable control technology currently available (BPCTCA)

TABLE XI-1
LOWEST DEMONSTRATED WASTEWATER FLOWS

Product Subcategory	cu meter/kkg	gal/1000 lbs
Alkyd molding compounds and unsaturated polyester resins	0.33	40
Cellulose nitrate	108	13,000
Ethylene-vinyl acetate	7.51	900
Polytetrafluoroethylene	33	4,000
Polyamides (Nylon 6/12 only)	6.7	800
Polyester resins - (thermoplastic)	7.9	950
Polypropylene fibers	1.67	200
Polyvinyl butyral	47	5,600
Silicones		
Fluids	10.4	1,250
Greases, Emulsions, Rubbers, Resins and Coupling Agents	100	12,000

requires considerable attention to both the process generation of waterborne pollutants as well as the water use practices of the plant.

Variability

The variability factors for BADT standards are based on the variability factors determined for BPCTCA for BOD_5 and COD. The TSS variability factors are 1.7 monthly and 2.5 daily as demonstrated by multi-media filtration data obtained from the petroleum industry. The other parameters are based on the achievable concentration for monthly maximum and a variability factor of 2 to determine the daily maximum.

Alkyds and Unsaturated Polyesters

The new source standards for alkyds and unsaturated polyesters are based on a process wastewater flow of 40 gal/1000 lbs of production as demonstrated by several plants within the subcategory. Since the flow basis for this subcategory is substantially lower than for any other subcategory in the plastics and synthetics industry, a brief description of how it is currently being attained is discussed below.

In the manufacture of alkyds and unsaturated polyesters, there are three main sources of process-related waste water:

1. Water of reaction
2. Scrubber water
3. Reactor cleanout water

(Surface condensers are assumed to be used instead of barometric type.)

Minimum discharge may be achieved by (1) reducing in-plant water usage through good housekeeping and water conservation practices, (2) recirculating scrubbing water until the concentration of organic material in that water is sufficiently high to allow for periodic incineration. If the organics are sufficiently concentrated the combustion may be self-supporting, (3) reusing reactor cleanout water to the maximum permissible, then combining it with the water of reaction, concentrating the blend by evaporation and sending the resulting waste to contract disposal.

Based on the factors discussed in this section, the New Source Performance Standards for Best Available Demonstrated Technology (NSPS-BADT) are presented in Tables XI-2 and XI-3.

TABLE XI-2

BEST AVAILABLE DEMONSTRATED TECHNOLOGY NEW SOURCE PERFORMANCE STANDARDS
[kg/kkg (lb/1000 lb) of production]

Foot-note No.	Subcategory	BOD$_5$		COD		Suspended Solids	
		Maximum Average of Daily Values for Any Period of Thirty Consecutive Days	Maximum for Any One Day	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days	Maximum for Any One Day	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days	Maximum for Any One Day
1	Ethylene-Vinyl Acetate Copolymers	0.18	0.35	1.8	3.5	0.13	0.29
2	Polytetrafluoroethylene	0.80	1.60	1.4	2.9	0.57	0.83
3	Polypropylene Fiber	0.04	0.08	0.07	0.14	0.03	0.04
4	Polyvinylidene Chloride	No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote	
5	Acrylic Resins	"	"	"	"	"	"
6	Cellulose Derivatives	"	"	"	"	"	"
7	Alkyds and Unsaturated Polyester Resins	0.02	0.03	00.11	0.20	0.006	0.008
8	Cellulose Nitrate	6.0	11	30	54	1.8	2.7
9	Polyamides (Nylon 6/12 only)	0.37	0.67	1.9	3.4	0.11	0.17
10	Polyester Resins (thermoplastic)	0.44	0.80	6.5	12	0.14	0.20
11	Polyvinyl Butyral						
12	Polyvinyl Ethers	No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote	
13	Silicones						
	Fluid	.57	1.0	4.7	8.5	0.18	0.26
	Greases, Emulsions, Rubbers, Resins, and Coupling Agents	5.5	10	45	82	1.7	2.5
14	Nitrile Barrier Resins	No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote		No numerical guidelines-see discussion in footnote	
15	Spandex Fibers	"	"	"	"	"	"

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FOOTNOTES FOR TABLES XI-2 and XI-3

1. Ethylene-Vinyl Acetate (EVA) Copolymer. Two of the five known producers were contacted. All plants are located at polyethylene production facilities. Water use and wastewater characteristics for EVA are essentially identical to these for low density polyethylene. However, an emulsion polymerization process is known and produces a distinctly different waste load which is essentially that of polyvinyl acetate emulsion polymerization reported in EPA 440/1-73/010. Both multi-plant and municipal sewage treatment is used.

2. Polytetrafluoroethylene. Three of the seven manufacturing plants were visited. A wide range of products are produced. The most important is polytetrafluorouthylene (PTFE) and these guidelines are recommended for PTFE granular and fine powder grades only. The wastewater discharges differ considerably depending upon the process recovery schemes for hydrochloric acid and the disposal of selected streams by deep well, ocean dumping or off-site contract methods. The use of ethylene glycol in a process can significantly affect the waste loads. Fluoride concentrations in untreated wastewaters are generally below lev ls attainable by alkaline precipitation.

3. Polypropylene Fibers. Two of the three producers were contacted. The volumetric flow ranges per unit of production vary widely depending upon the type of cooling system used. The waste loads are for plants where selected concentrated wastes are segragated and disposed of by landfilling, etc. Primary treatment at one plant site was observed while the other plant discharges to a municipal sewage system.

4. Polyvinylidene Chloride. The two major manufacturers were contacted. Both plant sites send wastewaters to multi-plant treatment plants of which the polyvinylidene chloride is a small portion. Consequently, there was insufficient data to develop recommended guidelines.

5. Acrylic Resins. Three of the four manufacturers were contacted. Large numbers of product grades are produced by bulk, solution, suspension and emulsion polymerization. The widely varying hydraulic loads for the large number of products in addition to treatment of the wastewaters by multi-plant wastewater treatment facilities prohibited obtaining sufficient meaningful data to recommend effluent limitation guidelines.

6. Cellulose Derivatives. Cellulose derivates investigated included ethyl cellulose, hydroxyethyl cellulose, methyl cellulose and carboxymethyl cellulose. Wide variations in unit flow rates for two plants producing the same product, differences in manufacturing techniques and the availability of data prevented recommending guidelines. The wastewaters from the three manufacturers are being treated in multi-plant wastewater treatment facilities or will enter municipal sewage systems.

7. Alkyds and Unsaturated Polyester Resins. Six carefully selected plants were visited to provide a cross-section of the industry for size of operation, type of manufacturing process and wastewater treatment methods. Hydraulic loads vary widely depending upon the process designs. Similarly, raw waste loads vary widely because some plants segragate wastes for disposal in other manners. Generally, the industry discharges wastewaters into municipal sewage systems and should continue. Also, the type of air pollution control, e.g. combustion or scrubbing, has a significant effect on the wastewater loads. The recommended guidelines are for plants having their own wastewater treatment system - a very infrequent occurrence.

8. Cellulose Nitrate. The two major manufacturers of the four manufacturers were contacted. These wastes require pH control and contain large amounts of ni..ates. One plant discharges to a municipal sewage system while the other goes into a multi-plant treatment complex.

9. Polyamides. Various polyamides are produced but only Nylon 6/12 produces significant amounts of wastewater, e.g. Nylon 11 uses no process water. Consequently, the guidelines are restricted to Nylon 6/12 and were developed on the basis of similarity with waste loads from Nylon 66 production.

10. Polyester Thermoplastic Resins. There are three manufacturers, two of which produce poly(ethylene, terephthalate) in quantities less than 2% of their total thermoplastic production. The guidelines are recommended for poly(ethylene terephthalate) since the other product poly(butylene terephthalate) is produced at only one plant and the wastewater goes into a municipal sewage system, so no data on performance could be obtained.

11. Polyvinyl butyral. Of three production sites, two have processes beginning with vinyl acetate monomer which generates much larger wastewater volumes than the process beginning with polyvinyl alcohol. Since the manufacturing sites where production starts with a monomer discharge into municipal sewage systems, there was no data available. Consequently, there are no recommended guidelines since they would be tantamount to establishing a permit for the direct discharger production site.

12. Polyvinyl ethers. The three present plants use different processes each of which produces several grades of product. The different chemical compositions used in both bulk and solution polymerization processes and the lack of data on both raw and treated wastewaters prevented establishing guidelines. The wastewaters are presently sent to either multi-plant treatment facilitie or municipal sewage systems.

13. Silicones. Four companies manufacture silicones at five locations. Three plants were visited and data were obtained from all plants. The major processing steps at the five plants are shown below.

Major Processes at Five Silicone Plants

Plant No.	1	2	3	4	5
CH_3Cl	x		x	x	
Chlorosilane prod.	x	x	x	x	x
Hydrolysis	x	x	x	x	x
Fluids, greases, emulsions prod.	x	x	x	x	x
Resin production	x	x	x		
Elastomer production	x	x	x		x
Specialties prod.*	x	x	x		
Fumed silica prod.			x		
HCl production					x

* e.g. surfactants, fluorinated silicones, coupling agents, and other materials.

Based on the manufacturing process, the waste water flows and the raw waste loads, the plants 1, 2, 3 and 5 were designated as multi-product plants while 4 was designated as a fluid product plant.

14. Nitrile Barrier Resins. Commercial scale production and sale of these resins has not yet begun. The companies expected to have production facilities were contacted, and two provided estimates of raw waste loads. Because of the lack of demonstrated flows and raw waste loads, it was impossible to establish effluent guideline limitations.

15. Spandex Fibers. Three manufacturers each produce Spandex fibers by significantly different processes. These are dry, wet and reaction spinning methods. Because of limited data on raw waste loads and because each plant operates a different process, it was impossible to establish meaningful guidelines.

TABLE XI-3

BEST AVAILABLE DEMONSTRATED TECHNOLOGY - NEW SOURCE PERFORMANCE STANDARDS
(Other Elements and Compounds)

Product	Parameter	kg/kkg (lbs/1000 lbs of Production) Maximum average of daily values for any period of thirty consecutive days	Maximum For Any One Day
Alkyds and unsaturated polyester resins			
	Mercury	Toxic and hazardous chemicals guidelines to apply	
Polytetrafluoroethylene	Fluorides	0.6	1.2
Spandex fibers	Cyanides	Toxic and hazardous chemicals guidelines to apply	
Nitrile barrier resins	Cyanides	" " "	" "
Polypropylene fibers	Oils and grease	0.017	0.034
Silicones			
Fluids	Copper	0.0026	0.0052
Greases, Emulsions, Rubbers, Resins and Coupling Agents	Copper	0.025	0.050
Polyester resins (thermoplastic)	mium	Toxic and hazardous chemicals guidelines to ap	

SECTION XII

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SECTION XIII

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SECTION XIV

GLOSSARY

Acetyl

Refers to that portion of a molecular structure which is derived from acetic acid.

Addition Polymerization

Polymerization without formation of a by-product (in contrast to condensation polymerization.)

Aerobic

A living or active biological system in the presence of free, dissolved oxygen.

Alkyl

A general term for monovalent aliphatic hydrocarbons.

Allophanate

A derivative of an acid, $NH_2CONHCOOH$, which is only known in derivative forms such as esters.

Alumina

The oxide of aluminum.

Amorphous

Without apparent crystalline form.

Anaerobic

Living or active in the absence of free oxygen.

Annealing

A process to reduce strains in a plastic by heating and subsequent cooling.

Aryl

A general term denoting the presence of unsaturated ring structures in the molecular structure of hydrocarbons.

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Atactic Polymer

A polymer in which the side chain groups are randomly distributed on one side or the other of the polymer chain. (An atactic polymer can be molded at much lower temperatures and is more soluble in most solvents than the corresponding isotactic polymer, g.q.).

Autoclave

An enclosed vessel where various conditions of temperature and pressure can be controlled.

Azeotrope

A liquid mixture that is characterized by a constant minimum or maximum boiling point which is lower or higher than that of any of the components and that distills without change in composition.

Bacteriostat

An agent which inhibits the growth of bacteria.

Blowdown

Removal of a portion of a circulating stream to prevent buildup of dissolved solids, e.g., boiler and cooling tower blowdown.

BOD5

Biochemical Oxygen Demand (5 days as determined by procedures in *Standard Methods*) 19th Edition, Water Pollution Control Federation, or EPA's Manual 16020-07/71, *Methods for Chemical Analysis of Water and Wastes.*

Catalyst

A substance which initiates primary polymerization or increases the rate of cure or crosslinking when added in quantities which are minor as compared with the amount of primary reactants.

Caustic Soda

A name for sodium hydroxide.

Chain Terminator

An agent which, when added to the components of a polymerization reaction, will stop the growth of a polymer chain, thereby preventing the addition of MER units.

COD

Chemical Oxygen Demand (determined by methods explained in the references given under BOD5.)

Copolymer

The polymer obtained when two or more monomers are involved in the polymerization reaction.

Cross-link

A comparatively short connecting unit (such as a chemical bond or a chemically bonded atom or group) between neighboring polymer chains.

Crystalline

Having regular arrangement of the atoms in a space lattice -- opposed to amorphous.

Delusterant

A compound (usually an inorganic mineral) added to reduce gloss or surface reflectivity of plastic resins or fibers.

Dialysis

The separation of substances in solution by means of their unequal diffusion through semipermeable membranes.

Diatomaceous Earth

A naturally occurring material containing the skeletal structures of diatoms - often used as an aid to filtration.

Effluent

The flow of waste waters from a plant or waste water treatment plant.

Emulsifier

An agent which promotes formation and stabilization of an emulsion, usually a surface-active agent.

Emulsion

A suspension of fine droplets of one liquid in another.

Facultative Lagoon or Pond

A combination of aerobic surface and anaerobic bottom existing in a basin holding biologically active waste waters.

Fatty Acids

An organic acid obtained by the hydrolysis (saponification) of natural fats and oils, e.g., stearic and palmitic acids. These acids are monobasic and may or may not contain some double bonds. They usually contain sixteen or more carbon atoms.

Filtration

The removal of particulates from liquids by membranes on in-depth media.

Formalin

A solution of formaldehyde in water.

Free Radical

An atom or a group of atoms, such as triphenyl methyl $(C_6H_5)_3C\cdot$, characterized by the presence of at least one upaired electron. Free radicals are effective in initiating many polymerizations.

Godet Roll

Glass or plastic rollers around which synthetic filaments are passed under tension for stretching.

GPD

Gallons per day.

GPM

Gallons per minute.

Halogen

The chemical group containing chlorine, fluorine, bromine, iodine.

Isotactic Polymer

A polymer in which the side chain groups are all located on one side of the polymer chain. See also "Atactic Polymer."

Lewis Acid

A substance capable of accepting from a base an unshared pair of electrons which then form a covalent bond. Examples are boron fluoride, aluminum chloride.

Homopolymer

A polymer containing only units of one single monomer.

Humectant

An agent which absorbs water. It is often added to resin formulations in order to increase water absorption and thereby minimize problems associated with electrostatic charge.

Influent

The flow of waste waters into a treatment plant.

M

Thousands (e.g., thousands metric tons).

MM

Millions (e.g., million pounds).

Monomer

A relatively simple compound which can react to form a polymer.

pH

A measure of the relative acidity or alkalinity of water on a scale of 0-14. A pH of 7 indicates a neutral condition, less than 7 an acid condition, greater than 7 an alkaline condition.

Phenol

Class of cyclic organic derivatives with the basic chemical formula $\mathrm{C6H5OH}$.

Plasticizer

A chemical added to polymers to impart flexibility, workability or distensibility.

Polymer

A high molecular weight organic compound, natural or synthetic, whose structure can be represented by a repeated small unit (MER).

Polymerization

A chemical reaction in which the molecules of a monomer are linked together to form large molecules whose molecular weight is a multiple of that of the original substance. When two or more monomers are involved, the process is called copolymerization.

Pretreatment

Treatment of waste waters prior to discharge to a publicly-owned waste water treatment plant.

Primary Treatment

First stage in sequential treatment of waste waters - essentially limited to removal of readily settlable solids.

Quenching

Sudden cooling of a warm plastic, usually by air or water.

Reflux

Condensation of a vapor and return of the liquid to the zone from which it was removed.

Resin

Any of a class of solid or semisolid organic products of natural or synthetic origin, generally of high molecular weight with no definite melting point. Most resins are polymers.

Scrubber

Equipment for removing condensable vapors and particulates from gas streams by contacting with water or other liquid.

Secondary Treatment

Removal of biologically active soluble substances by the growth of microorganisms.

Slurry

Solid particles dispersed in a liquid medium.

Spinnerette

A type of extrusion die consisting of a metal plate with many small holes through which a molten plastic resin is forced to make fibers and filaments.

Staple

Textile fibers of short length, usually one-half to three inches.

Stoichiometric

Characterized by being a proportion of substances exactly right for a specific chemical reaction with no excess of any reactant or product.

TDS

Total dissolved solids - soluble substances as determined by procedures given in reference under BOD_5.

Thermoplastic

Having property of softening or fusing when heated and of hardening to a rigid form again when cooled.

Thermosetting

Having the property of becoming permanently hard and rigid when heated or cured.

TOC

Total Organic Carbon - a method for determining the organic carbon content of waste waters.

Tow

A large number of continuous filaments of long length. Tow is the usual form of fibers after spinning and stretching and prior to being chopped into short lengths of staple.

Transesterification

A reaction in which one ester is converted into another.

Vacuum

A condition where the pressure is less than atmospheric.

Ziegler-Natta Catalyst

A catalyst (such as a transition metal halide or an organometallic compound) that promotes an ionic type of polymerization of ethylene or other olefins at atmospheric pressure with the resultant formation of a relatively high-melting polyethylene or similar product.

TABLE XIV-1

METRIC TABLE

CONVERSION TABLE

MULTIPLY (ENGLISH UNITS) by TO OBTAIN (METRIC UNITS)

ENGLISH UNIT	ABBREVIATION	CONVERSION	ABBREVIATION	METRIC UNIT
acre	ac	0.405	ha	hectares
acre - feet	ac ft	1233.5	cu m	cubic meters
British Thermal Unit	BTU	0.252	kg cal	kilogram - calories
British Thermal Unit/pound	BTU/lb	0.555	kg cal/kg	kilogram calories/kilogram
cubic feet/minute	cfm	0.028	cu m/min	cubic meters/minute
cubic feet/second	cfs	1.7	cu m/min	cubic meters/minute
cubic feet	cu ft	0.028	cu m	cubic meters
cubic feet	cu ft	28.32	l	liters
cubic inches	cu in	16.39	cu cm	cubic centimeters
degree Fahrenheit	°F	0.555(°F-32)*	°C	degree Centigrade
feet	ft	0.3048	m	meters
gallon	gal	3.785	l	liters
gallon/minute	gpm	0.0631	l/sec	liters/second
horsepower	hp	0.7457	kw	killowatts
inches	in	2.54	cm	centimeters
inches of mercury	in Hg	0.03342	atm	atmospheres
pounds	lb	0.454	kg	kilograms
million gallons/day	mgd	3,785	cu m/day	cubic meters/day
mile	mi	1.609	km	kilometer
pound/square inch (gauge)	psig	(0.06805 psig +1)*	atm	atmospheres (absolute)
square feet	sq ft	0.0929	sq m	square meters
square inches	sq in	6.452	sq cm	square centimeters
ton (short)	ton	0.907	kkg	metric ton (1000 kilograms)
yard	yd	0.9144	m	meter

* Actual conversion, not a multiplier

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